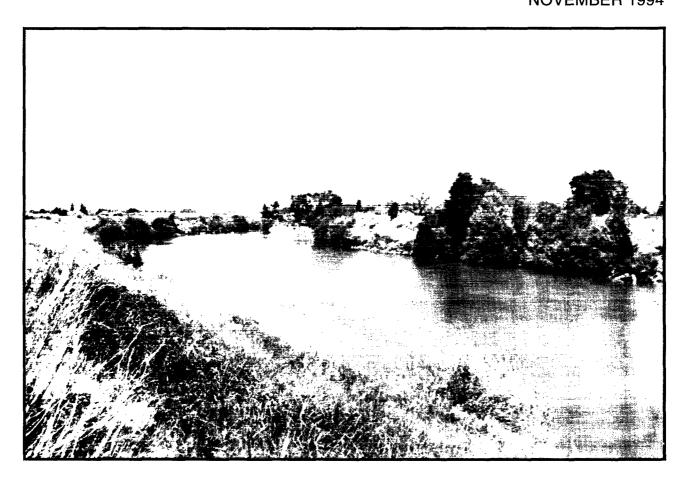
State of California
The Resources Agency
Department of Water Resources
Division of Local Assistance

FIVE-YEAR REPORT OF THE MUNICIPAL WATER QUALITY INVESTIGATIONS PROGRAM

Summary and Findings During Five Dry Years January 1987-December 1991 NOVEMBER 1994



Douglas P. Wheeler Secretary for Resources The Resources Agency Pete Wilson Governor State of California David N. Kennedy Director Department of Water Resources

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FOREWORD

In 1990 the Department of Water Resources consolidated its drinking water quality studies in the Sacramento-San Joaquin Delta. The Intergency Delta Health Aspects Monitoring Progam (1983-89), the Delta Islands Drainage Investigation (1986-89), and ancillary studies were combined into the Municipal Water Quality Investigations (MWQI) Program.

The program's major goal is to assist water agencies in protecting and improving Delta drinking water supplies and to guide research into methods of water treatment. To achieve this, program staff examine the major sources and causes of water quality changes in the Delta that affect drinking water quality. Key Delta channel and river stations and agricultural drains are monitored for contaminants such as pesticides, arsenic, selenium, sodium, and trihalomethane formation potential.

Californians experienced a six-year drought starting in 1987 that resulted in severe water shortages to some communities. As a result, water agencies implemented water conservation programs and emergency contingency plans. With less river flow into the Delta, sea water intrusion was more extensive. Delta farming changed in 1991 with less crop acreage than previous years. Delta farmers sold about half of their water allocation to the State Water Bank to help maintain domestic supplies, and about one-third of the Delta acreage was not farmed. Therefore, water quality conditions observed in the Delta represented rare and extreme dry weather hydrology.

This report presents the findings from monitoring water quality changes in the Delta during January 1987 to December 1991, a period of five consecutive dry years.

For further information on the Municipal Water Quality Investigations Program, contact Rick Woodard of the Division of Local Assistance, Department of Water Resources, at (916) 327-1636. Limited copies of this report can be obtained at no charge from Bulletins and Reports, Department of Water Resources, Post Office Box 942836, Sacramento, California 94236-0001, phone: (916) 653-1097.

Carlos Madrid, Chief

Division of Local Assistance

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ORGANIZATION

State of California
PETE WILSON, GOVERNOR

The Resources Agency DOUGLAS P. WHEELER, Secretary of Resources

Department of Water Resources DAVID N. KENNEDY, Director

John J. Silveira Deputy Director Robert G. Potter Chief Deputy Director

Carroll M. Hamon Deputy Director

L. Lucinda Chipponeri Assistant Director for Legislation Susan N. Weber Chief Counsel

DIVISION OF LOCAL ASSISTANCE Carlos Madrid, Chief

Water Quality Assessment Program Richard P. Woodard, Staff Toxicologist

Bruce Agee
Program Management

Michael Sutliff Field Operations

Lori Weisser

Data Management

Judith Heath

QC/QA Management

Marvin Jung

Analysis & Reporting

With assistance from Cassandra Enos, David Gonzalez, Walt Lambert, Kathy Mata, William J. McCune, Nan Singhasemanon, Kenley Ngim, Sanjib Sah, and technical editor Lynda Dale Herren.

Data analysis, interpretation, and report by Marvin Jung & Associates, Inc. of Sacramento under DWR contract B-56213. Contributors included B.J. Archer, P.E. (DWR retired annuitant) for the mass loading estimates, Bruce Agee for the TFPC assay method, Judith Heath, Cassandra Enos, Nan Singhasemanon, and Sanjib Sah for the data quality assessment.

Chapter 1. EXECUTIVE SUMMARY

Municipalities taking water from the Sacramento-San Joaquin Delta are currently faced with an array of challenges. Besides having to compete for increasingly scarce water supplies, new State and federal drinking water regulations are requiring increasing levels of treatment. The cost of treating Delta waters to meet some anticipated new standards could be staggering. For this reason there is great interest in gathering water quality information from the Delta to assist in water treatment and water supply planning and research.

Under the Department of Water Resources' Municipal Water Quality Investigations (MWQI) Program, the quality of the Delta's drinking water supplies has been monitored since 1982. Over 70 sites are sampled, many of which are sampled each month, and special studies are

Monitoring is vital for water resources planning and water quality research, especially in view of changing environmental and drinking water regulations.

conducted to gather information for the use of municipalities taking water from the Delta, and for planning activities within the Department. The monitoring stations include agricultural drainage discharge sites, major river channels and sloughs, estuarine locations, and water intakes or diversions (Figures 1.1 and 1.2).

Special emphasis has focused on identifying the sources and processes that enhance the formation of disinfection byproducts in treated Delta water supplies. Disinfection, which is critical to protect against microbial disease, also produces

chemical by-products that may pose other health risks such as cancer. Trihalomethanes (THMs) are some of the types of disinfection by-products (DBPs) that can be formed.

Until recently, trihalomethanes were the only regulated DBPs (0.100 mg/L), and chlorine and chloramines were the preferred disinfectants of choice because of lower costs and high effectiveness in controlling bacterial growth in the water distribution system. However, new U.S. Environmental Protection Agency regulations, which take effect in 1998 and referred to as the Disinfectants-Disinfection By-Products or D-DBP rule, have caused water utilities to initiate research on water treatment technologies such as ozonation and granular activated carbon filtration, and to expand their chemical testing for additional DBPs.

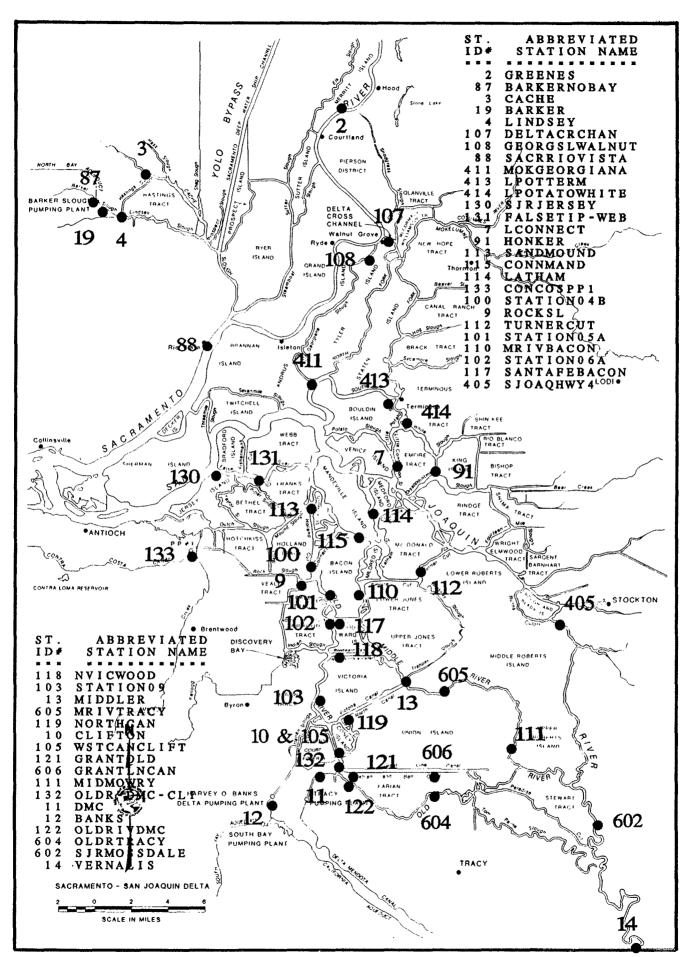


Figure 1.1. Monitored Channel Stations

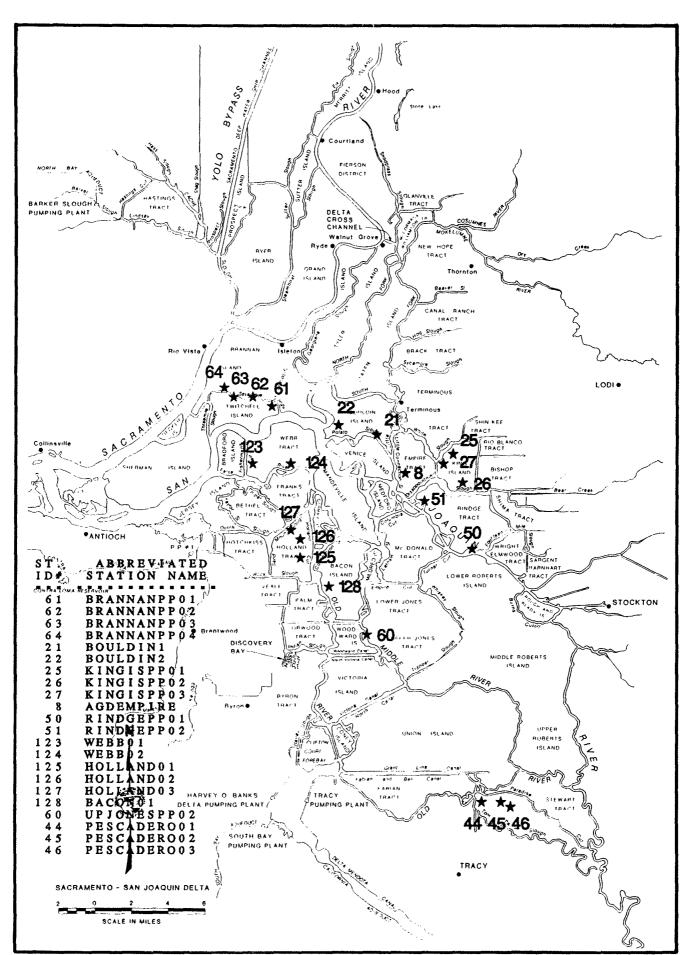


Figure 1.2. Monitored Agricultural Drainage Pump Stations

While control of DBPs is important, water purveyors must also consider that the primary thrust of disinfection is to control waterborne disease. Recent outbreaks in Milwaukee, Wisconsin, and Washington, DC, have demonstrated that, in relatively unprotected watersheds, like the Delta, disease is a considerable threat. Purveyors are, therefore, faced with maintaining a delicate balance of maintaining adequate disinfection while limiting formation of unwanted byproducts. Because Delta waters have elevated concentrations of organic matter and bromides, which contribute to formation of DBPs, finding an appropriate balance between these competing factors is especially difficult.

The new D-DBP rule has two stages. Stage 1, effective June 1998, will lower the total THM standard from 0.100 mg/L to 0.080 mg/L. Limits will be set for other DBPs including

Prior to the new rule, THMs were the only regulated DBPs. bromate (0.010 mg/L), chlorite (1.0 mg/L), and the sum total concentration of five specified haloacetic acids, referred to as the "HAA5" (0.060 mg/L). Limits for the disinfectant residuals of chlorine, chloramines, and chlorine dioxide must also be met.

The best available technology (BAT) for meeting the stage 1 maximum contaminant levels (MCL) for total THMs and the HAA5 are enhanced coagulation, enhanced softening, or granular activated carbon (GAC). The BAT for meeting the bromate MCL will consist of controlling ozonation. Control of the chlorine dioxide process will be the BAT for meeting the chlorite MCL. Since extensive research, retrofitting, and upgrading of treatment facilities will be needed to meet the new rule, stage 1 of the rule will not be in effect until June 1998.

Stage 2 of the D-DBP rule may, subject to renegotiation, further lower the total THM MCL to 0.040 mg/L and the HAA5 MCL to 0.030 mg/L. Stage 2 of the rule takes effect in January 2002.

The degree of success water utilities will experience in complying with the new DBP rule will depend, in part, on how well DBP precursors (chemicals that lead to the formation of DBPs) can be reduced in the raw water supply prior to disinfection. By removing these precursors, the

Meeting DBP MCLs
will, in part, depend on
how well a water
treatment plant can
control bromide and
organic matter in the
water prior to adding
disinfectant
chemicals.

formation of known and unknown DBPs can be lowered. Changing or reducing the amount of

disinfectants may reduce formation of some DBPs but may also raise the risk for waterborne disease outbreaks such as cholera.

The major precursors that have been identified as needing to be controlled are organic matter and bromide. Some parts of the Delta, the south in particular, have high concentrations of bromide and organic matter. Waters diverted by the State Water Project, Central Valley Project, and Contra Costa Water District are generally higher in organic matter, bromide, and other mineral salts than the waters of the northern Delta. Sea water has been traced as the major source of bromides in the southern Delta.

There are, however, many sources of organic matter. Some of them include streamside vegetation, decaying crop residues, algae, and sewage. The largest source appears to be from the region's soils. Because the Delta was once a vast tule marsh and is now mostly farm land, the soils of the region are rich in organic material from decaying marsh and crop residues.

About 260 pump stations are dispersed among 60 Delta islands and tracts that are below sea level. The pumps discharge a combination of seepage, runoff, and irrigation return water into the adjacent channels. Drain water is high in mineral salts and organic matter. The salts come from the evaporation of irrigation water. However, in some areas, such as Empire Tract, connate water from an underground marine aquifer contributes mineral salts to the drainage.

The volume and water quality of drain water that is discharged into the channels correlate with the seasonal farming activities and regional soils (Figure 1.3). There are two periods when drainage volumes are highest. In the late fall and early winter, the fields are flooded to leach out salt accumulations from the soil. This results in short periods of high drainage volume and high dissolved organic carbon (DOC) concentrations in the drainage, especially from organic soil areas.

Seasonal farming activities affect the amount of organic matter that is carried off by drain water.

High DOC and trihalomethane formation potential (THMFP) levels are associated with the organic content of the drained soils. The highest concentrations are typically found in drains located on peat organic soil areas and the lowest from mineral-type soil areas. U.S. Geological Survey studies attribute the variability in DOC at a given site to soil-water contact time,

water table height, soil moisture, and temperature (Deverel and others, 1993).

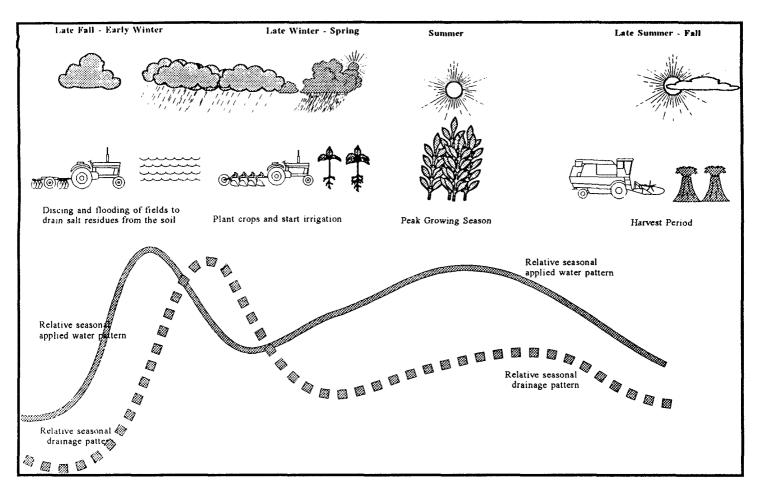
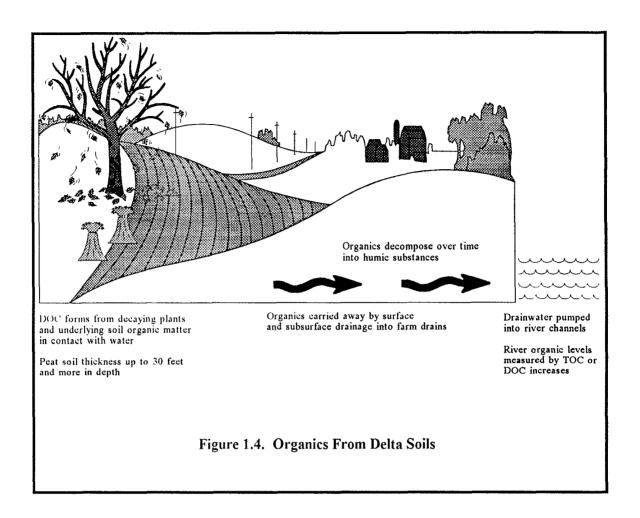


Figure 1.3. Seasonal Farming Activities in the Delta

The second peak drainage season occurs during the summer when irrigation is increased. DOC levels are relatively lower than when the fields are leached in the late fall and early winter. This may be caused by less soil to water contact time and a fluctuating lower water table that reduces the soil moisture.

Drain water has a greater tendency to form trihalomethanes and other disinfection byproducts when chlorinated than nondrain water samples. This is due to the high humic content of the region's peat soil.

Humic substances form from the progressive decay of natural organic matter (Figures 1.4 and 1.5) and are considered to be the complex mixture of organic compounds that are DBP precursors. The discovery of trihalomethanes in treated drinking water resulted from a study on the effects of chlorinating humic substances (Rook, 1974).



The increases in DOC and THM precursor concentrations in the Delta channel waters are mostly from drainage discharges.

The high DOC and THM formation potential of Delta drain water is not surprising. Natural waters from organically enriched environments such as bogs, marshes, and wetlands are typically higher in DOC and humic content than sea water and most streams and lakes.

Based on past drainage volume estimates (1954-55) and more recent monitoring data assessments (1983-93),

the increases in DOC and THM precursor concentrations in the Delta channel waters are mostly from drainage discharges. Some increases are due to activities within the channel, such as dredging, sediment leaching, and biological productivity, but they are relatively smaller than from drainage discharges. An estimate of the contribution of THMFP for Delta island drainage was published in the DWR *Delta Island Drainage Investigation Report*, *June 1990*.

Water quality at the intakes of the State and federal water projects generally does not resemble that of Sacramento River inflows to the Delta except when river flows are extremely high, such as during strong winter storms. During low river flows, water quality at the Tracy Pumping Plant and Clifton Court Forebay gates is affected by daily tidal excursions, Sacramento River flows that control the extent of salt water intrusion, and San Joaquin River flows entering the southern Delta.

During calendar years 1987-91, most of the low San Joaquin River flows were drawn into the Delta-Mendota Canal intake. Sacramento River flows at Greenes Landing were generally ten times greater than San Joaquin inflows near Vernalis. Some of the Sacramento River flow was drawn through the central and western Delta into the State Water Project and Delta-Mendota Canal. The Sacramento River was virtually the sole fresh water source for the entire Delta.

A summary of observed EC, bromide, DOC, THMFP, and TFPC concentrations across the Delta during the five-year period are graphically summarized in notched box-and-whisker plots (Figures 1.7-1.11). An explanation of notched box-and-whisker plots is presented in Figure 1.6.

These plots are a method for graphically showing how the data are distributed. The positions of the end points and notches give information on the extreme high and low values, the median, and the range of values by quartiles. It provides an overview as to whether the observations are widely scattered or not. The figures are useful for studying the variability of observations. The information is also useful for selecting representative data for a site.

The median electrical conductivity (EC), which is also called specific conductance, at the American River WTP intake station (AMER on Figure 1.7) was about 75 μ S/cm and about 175 μ S/cm at Greenes Landing (GRN). The median EC at Little Connection Slough (LCON) near Empire Tract was about 240 μ S/cm. Increases in EC values were evident downstream at the other Delta stations influenced by drainage and seawater. The high EC (median 850 μ S/cm) at Vernalis (VRN) reflected the upstream agricultural drainage discharges into the San Joaquin River.

Figure 1.5. The Transformation of Natural Organic Matter

Particulate organic carbon (POC) such as plant litter in contact with water decomposes and dissolves.

Approx. concentrations (mg/L) of DOC and POC in natural waters Delta DOC ranges (mg/L) DOC POC 2 - 3 Sacramento River 0.5 .1 sea water 3 - 4 San Joaquin River 5 - 6 0.7 .1 ground water Banks Pumping Plant .1 precipitation 10 - 20 Peak stormwater runoff 10 - 20 Mineral soil drainage 2 oligotrophic lake 2 river 10 - 80 Peat soil drainage 10 2 eutrophic lake 15 2 marsh 3 bog Dissolved organic matter (DOC) formed and microbially degraded water, ammonia, carbon dioxide, + methane gases Humic substances (UV absorbing compounds and known THM precursors Non-humic compounds such as humic and fulvic acids) Percent of DOC as humic substances for different water types 25% sea water 25% DOC operationally defined as organic matter ground water 34% lakes that passes through a 0.45 micron pore sized 47% streams and rivers filter. POC is larger than 0.45 microns. 75% wetlands

The 700 μ S/cm EC median at Rock Slough near Old River (ROCK) is attributed to multiple sources, including sea water, Delta island drainage, and water from the San Joaquin River . The median EC values of water at the Banks Headworks (BANK), Clifton Court Forebay intake gates (CLIF), and DMC intake (DMC) stations were about 550 to 600 μ S/cm and are attributed to mixing with lower EC water from Middle River (MIDR; median 450), which joins Old River at three canals between Bacon Island and Union Island.

Southern Delta water samples were higher in bromide than those from the northern Delta region (Figure 1.8). Bromide sources include sea water, connate water from Delta islands, and San Joaquin River basin drainage.

New total organic carbon (TOC) limits (2 mg/L) under the D-DBP rule will require enhanced coagulation or enhanced softening prior to disinfection for conventional water treatment plants (coagulation, flocculation, sedimentation, and filtration) and softening plants. The percent of TOC removal required by enhanced coagulation will depend on the source water TOC and alkalinity. Unfortunately, bromide, which leads to the formation of bromate and brominated THMs, will not be reduced by technologies to remove TOC. For this reason, utilities are also looking at other disinfectants such as ozone. However, there are concerns that these other

TOC levels at some Delta water intakes already approach the new D-DBP rule limit and may require TOC reduction at some treatment plants

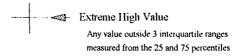
disinfectants may form other DBPs that may be regulated in the near future.

Delta TOC data are limited, but dissolved organic carbon (DOC) data are available for comparison. Past work has shown Delta DOC levels to be about the same as TOC levels. The median DOC concentrations at Greenes Landing and the American

River stations were about 2 mg/L (Figure 1.9). Downstream median DOC was generally over 3 mg/L and had a wider range of concentrations. DOC usually doubles during the wet, rainy season from heavy surface runoff and drainage. Major storms can increase DOC even more during peak runoff periods.

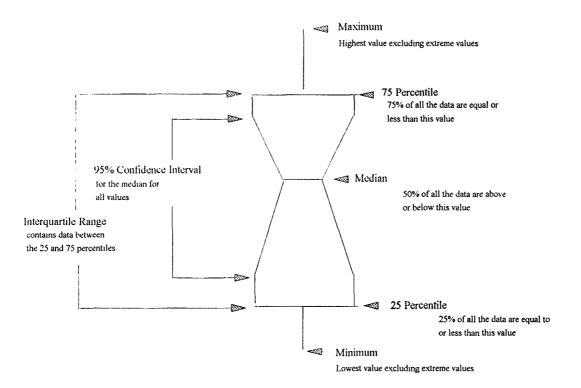
Figure 1.6.

Guide to Notched Box-and-Whisker Plots

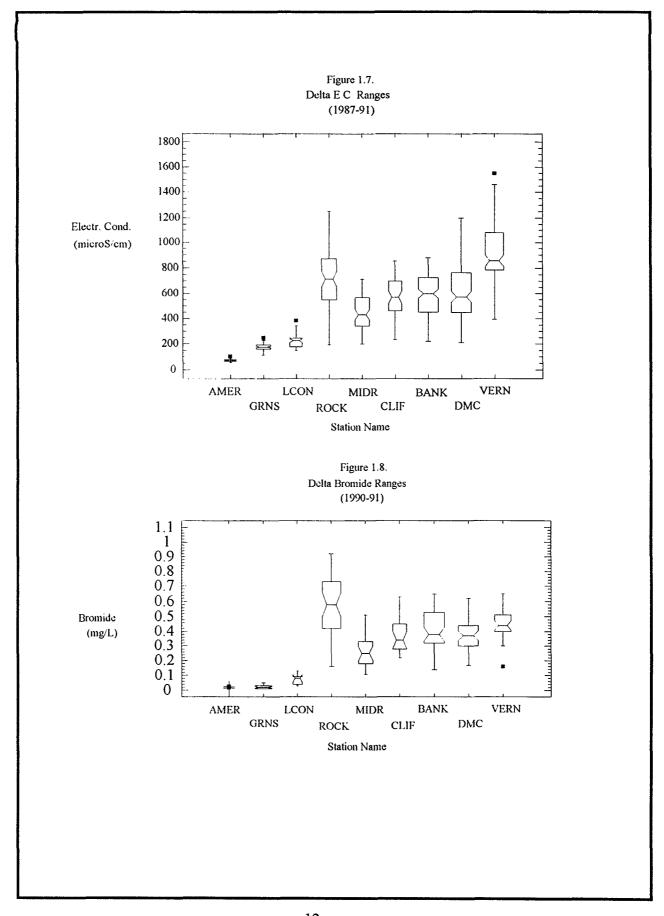


Upper High Value

Any value outside 1.5 interquartile ranges measured from the 25 and 75 percentiles



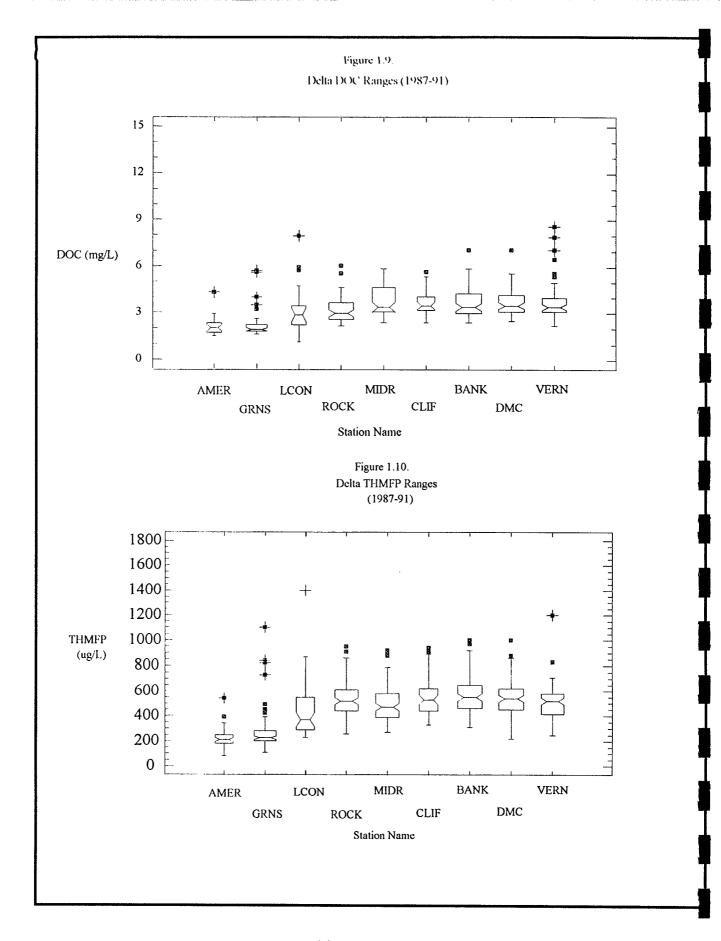
NOTE: Horizontal width of box is proportional to the square root of the sample size



Trihalomethane formation potential, based on the DWR THMFP assay for raw water, was two to three times higher in the southern Delta than at Greenes Landing and the American River (Figure 1.10). However, these results are not comparable to the actual amount of trihalomethanes formed at a treatment plant after disinfection. Since different treatment schemes are used to limit THM formation, DWR results cannot be equated to actual THM concentrations found in tap water. The DWR raw water assay was established for comparing the THM formation potential of the variety of water types in the Delta, some of which are never used as a drinking water source (e.g., drain water, sea water).

To distinguish THMFP concentrations caused by bromide from that caused by reactive organic material, the amount of organic carbon from the THMFP concentrations was computed to yield the trihalomethane formation potential carbon (TFPC) concentration. This is a measure of how much carbon was incorporated in the trihalomethanes that were formed in the THMFP assay. The distribution pattern of Delta TFPC data was similar to the THMFP data for most stations (Figure 1.11).

The DWR THMFP assay results do not represent the amount of trihalomethanes found at the consumer's tap. It is a measure of the relative potential of different water types to form THMs. It is a tool for identifying sources of THM precursors.



A simple accounting model was used to estimate the impact of organic carbon from drainage and nondrainage sources. Observed average DOC and TFPC concentrations were compared to predicted average values that were computed from 1954-55 drainage volume data (DWR, 1956), available water quality data, and river flow measurements. The model treated the Delta as a basin and assumed that the mathematical difference between the observed Delta concentrations and the predicted increase from drainage came from in-channel sources (e.g., algae).

Example simple model predicted estimate:

Observed Delta DOC value = 3.5 mg/L

Predicted Delta DOC value from

island drainage = 3.4 mg/L

Observed river DOC inflow

value = 2.5 mg/L

Therefore,

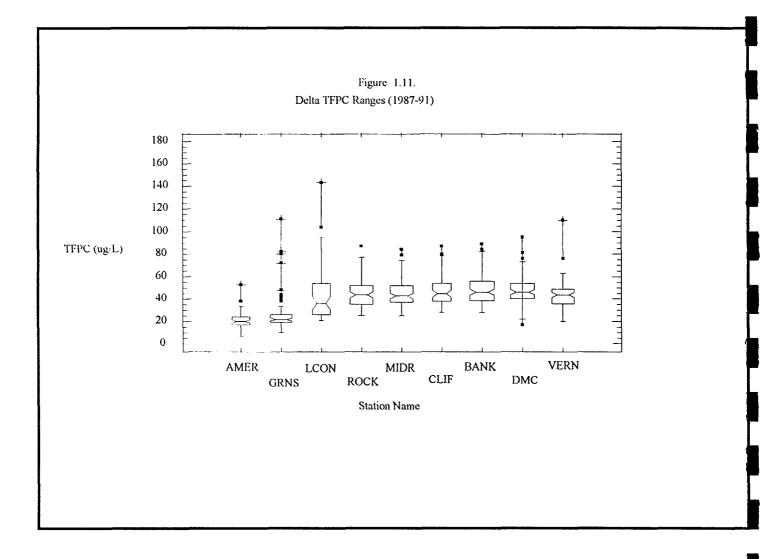
From in-channel sources = 3.5 - 3.4 = 0.1 mg/L DOC

From drainage sources = 3.4 - 2.5 = 0.9 mg/L DOC

Overall, the results showed that the impacts from drainage and in-channel sources could not be fully distinquished. The outcome of the results was affected by the drainage volume estimates and the available water quality data that served as representative monthly averages for island drain water and the Delta channels.

The model showed an average increase of 1.1 mg/L DOC in the Delta from the average river concentration of 2.5 mg/L. The model results for DOC, however, were best when the drainage volume was assumed to be 10 percent higher than the 1954-55 estimates. This could mean that current island drainage is 10 percent higher than 40 years ago or that it has remained the same but the 10 percent increase is caused by in-channel sources.

Similarly, the model accounted for a 56 percent increase in TFPC from drainage when the observed Delta TFPC was 79 percent higher. This could indicate a 23 percent increase from inchannel sources or an underestimation due to the DWR THMFP assay for drain water samples with more than 20 mg/L DOC. In all cases, the importance of gathering new drainage volume information was shown. Improvements in the simplified model are expected as new monitoring



Revised estimates on the amount of drain water entering the channels will help assess the contribution of organics from drainage as well as from other Delta sources. data are collected.

The Department's Division of Planning is using data from the MWQI Program to develop a Delta THM computer model. The model combines the Department's existing Delta Simulation Model (DSM), which mimics the complex hydrology of the estuary to predict water quality in the Delta, with a THM model component. This component uses output from the DSM and data on water treatment conditions to simulate the formation of THMs. When completed, the Delta

THM computer model will assist the agency in studying proposed water management strategies such as new Delta facilities, drainage management, and regulatory actions.

Two improvements in THM precursor measurement have been initiated in recent years. A

The prediction of THM formation is now an important part of DWR's Delta modeling efforts.

modified chemical testing procedure was developed and adopted in 1992 to improve measurement of the organic THM precursor carbon concentrations in high DOC water samples. This was needed because the original DWR THMFP assay method was shown to underestimate the

precursor level in some high DOC water (above 20 mg/L) samples such as drain water. Starting

in 1990, water samples were also measured for ultraviolet absorbance (UVA $_{254\text{nm}}$). This measurement is used as another indicator of THM precursors and correlates well with DOC for most water samples. This provides a quick and inexpensive measurement useful in assessing the THM precursor levels in the Delta.

Improved methods to measure the amount of THM precursor organic carbon in the Delta are being studied.

Staff of the Department's Quality Assurance and Quality Control Program participated in an analysis of the MWQI field and laboratory data. The review identified the need to establish uniform laboratory reporting procedures, routine laboratory data review protocols, and incorporation of the information in a computer database.

There continues to be significant progress in understanding the sources and nature of organic THM precursors in the Delta. Statistical analyses of the data showed some good correlations among location, soil types, and some water quality measurements such as UVA, DOC, bromide, and chloride. This information is used to develop estimates of the quality of drain water and channel water at unmonitored sites.

Planned activities include new studies to help reduce organics and bromide in Delta water supplies and to improve the monitoring and assessment methods. The following studies are planned or are in progress:

- DWR will compare data from 1992-93 to predicted results of the mathematical relationships of UVA, DOC, and THMFP that were seen in the 1987-91 data. The information will improve modeling efforts to predict regional DOC and THMFP.
- 2. DWR and the U.S. Geological Survey will conduct a joint study to measure the

irrigation and drainage water quantities, quality, and power use for pumping drain water off the islands. Several islands, representative of different soil types and crop patterns in the Delta, will be studied.

3. DWR will draft proposed studies to examine the impacts of alternative land uses

and changes in field irrigation and leaching practices on crop production, drainage volume, water quality, and electrical power savings.

4. DWR will study with the use of automated sampling devices, daily and hourly variations in water quality at channel stations affected by tides and at drainage pump stations.

Simple changes in land use and leaching practices need to be studied as potential methods for reducing TOC without impairment to agriculture.

- 5. DWR will review the need for current and future monitoring and special studies. New monitoring stations may be established at tributaries flowing into the Delta for studying upstream sources of DBP precursors.
- 6. DWR will continue to refine the Delta THMFP computer model.
- 7. DWR will collect and compare data from more water year types. The majority of water years that have been monitored since 1982 were below normal and critically dry water type years. Therefore, the 1987-91 observations and interpretations reflect an unusual period of five consecutive drought years.
- 8. DWR will adopt recommendations for improving the management and review of laboratory quality assurance and quality control data.

In addition to the new D-DBP rule, an Enhanced Surface Water Treatment Rule (ESWTR) and Information Collection Rule (ICR) will be issued. The EWSTR focuses on removing or inactivating disease-causing microoganisms such as *Giardia lamblia*, *Legionella*, *Cryptosporidium*, and viruses. The ICR requires gathering extensive monitoring and treatment data to establish the EWSTR and stage 2 of the D-DBP rule. The MWQI Program will work

The MWQI Program will respond to new and future data collection needs.

with the program advisors in broadening its monitoring efforts to gather needed information for these and forthcoming data collection requirements.

In summary:

- Monitoring data from the MWQI program has been important for water resources planning and water quality research, especially in view of changing environmental and drinking water regulations.
- Prior to the new EPA Disinfectant-Disinfection Byproducts (D-DBP) rule, tribalomethanes were the only DBPs regulated in drinking water.
- Meeting the new DBP regulations will depend, in part, on how well precursors such as bromide and organic matter can be reduced in the water prior to adding disinfectant.
- ◆ The major Delta water supplies receive high concentrations of bromide from bay water and organics from its tributaries and from within the Delta. Most Delta soils are rich in organic matter from decomposing peat soil and crop residues.
- Seasonal farming activities affect the amount of organic matter leached and drained from the island soils and eventually discharged into the Delta channels.
- → The high THM formation potential and DOC found in some parts of the Delta are typical for the area, because the Delta was a vast tule marsh prior to being reclaimed a hundred years ago.
- TOC reduction at some treatment plants will be required to meet the new D-DBP rule because of high TOC in some Delta water supplies.

- Revised estimates on the volume of drain water entering the channels will help assess the contribution of organic material from drainage as well as from other sources.
- ◆ DWR's Delta modeling section has developed a Delta THM computer model to assist in water resources and facilities planning.
- ▶ New activities focus on ways of updating drainage volume and quality estimates, refining monitoring and assessment methods, and streamlining quality assurance and quality control evaluations.
- ◆ The MWQI program will respond to new and future data collection requirements and needs.

Chapter 2. PROGRAM DESCRIPTION

Objectives

Waters of the Sacramento-San Joaquin Delta serve nearly 20 million people living in the Bay-Delta region and Southern California; the supply is, therefore, extremely important to the health and economy of the State.

In 1982, a DWR scientific advisory panel recommended that a Delta water quality monitoring program focusing on human health concerns be established. This recommendation was made because knowledge about the quality of Delta drinking water supplies was limited. The panel expressed concerns about pesticides, asbestos, sodium, and trihalomethane precursors. In 1983, DWR began the recommended monitoring program and special studies. The program was called the Interagency Delta Health Aspects Monitoring Program (IDHAMP). In 1987, the Delta Island Drainage Investigation (DIDI) was established to gather information to evaluate the effects of agricultural drainage on channel water quality.

DWR established the Municipal Water Quality Investigations (MWQI) Program in 1990. The MWQI Program unified the agency's drinking water quality studies in the Sacramento-San Joaquin Delta. The studies included the earlier IDHAMP (1983-89), the former DIDI (1986-89), and special studies to monitor bromide and sea water intrusion (1989).

Program staff monitor and assess water quality changes in the Delta. These changes are caused by natural processes and man-made activities within the tidal estuary, including shifts in river inflows, agricultural drainage, and weather-related events.

The data are used to:

- (1) Alert water agencies about potential contaminant sources to Delta water supplies;
- (2) Document water quality under a variety of hydrologic conditions for studying water transfer alternatives, water quality standards, and predictive modeling capabilities;
- (3) Determine the influence of sea water intrusion, local and external sources of farm drainage, river inflow, in-channel processes, weather, and State Water Project and Central Valley Project operations on Delta drinking

water quality (selenium, bromide, and other inorganic constituents are used to trace the movement and mixing of water from different sources.); and

(4) Assist water agencies in planning, protecting, and improving drinking water facilities and treatment techniques.

Over the years, several water-borne contaminants and pollutants have been monitored, including asbestos, salts, arsenic, selenium, pesticides, and trihalomethane precursors. Special sampling runs are made when additional water quality concerns arise.

By examining monitoring data, MWQI staff gains an understanding of the shifts in water quality during a variety of environmental conditions and water management operations.

Data from this study are being used to examine the most cost-effective solution for meeting new EPA drinking water standards. This information is also needed by the State Water Resources Control Board (SWRCB) for setting water quality objectives in the Delta to meet and protect the competing beneficial uses of the Delta. These include agricultural, fisheries, recreational, municipal, and industrial uses. The economic importance and value of each of these beneficial uses have been presented by various parties before the SWRCB during the 1987-90 Bay-Delta hearings.

In summary, MWQI data are used for the planning and protecting Delta water resources. This report covers monitoring results from January 1987 through December 1991, five consecutive dry years.

Participants

The MWQI study is a component of DWR's Water Quality Assessment program, which is managed by the Division of Local Assistance. A project team of environmental specialists, engineers, and water quality technicians manage and coordinate the MWQI studies.

Advice on the program's direction and technical expertise is provided by three committees (Table 2.1). A Municipal Water Quality Advisory Group and Technical Subcommitee provide close coordination and communication between the MWQI staff and major water agencies and regulatory agencies. The Advisory Group provides information about regional water quality and treatment concerns that may necessitate further monitoring or special studies. The Technical Subcommittee provides invaluable expertise on the latest analytical methods, water treatment practices, proposed drinking water standards, and the interpretation of monitoring data. A Delta Lands Advisory Group assists DWR in gaining access to sample agricultural drainages in the Delta, provides information about farming operations and practices that may affect Delta water use, and reviews project reports.

Table 2.1. Program Advisors

Participating agencies during 1987-91 included:

Municipal Water Quality Advisory Group and Technical Subcommittee

Alameda County Flood Control and
Water Conservation District, Zone 7
Alameda County Water District
California Department of Water Resources
California Department of Health Services
California Urban Water Agencies
Contra Costa Water District
East Bay Municipal Utility District
Los Angeles Department of Water and Power
The Metropolitan Water District of Southern California
Santa Clara Valley Water District
State Water Contractors
U.S. Environmental Protection Agency

<u>Delta Lands Advisory Group</u> (formerly Delta Islands Drainage Investigation Technical Advisors)

California Central Valley Flood Control Association
Murray, Burns, and Kienlen Engineers
Reclamation District 38
Reclamation District 1004
Reclamation District 2068
Reclamation District 2075 and
South Delta Water Agency

Monitoring Stations

Monitoring stations are established to meet the data needs of the participating agencies. Key stations include channels leading to public water supply intakes and drainages from Delta islands and tracts having major soil types of the region. Other stations are located in the Delta channels and rivers. Data collected at these stations help provide a more complete picture about flow patterns and water quality changes during certain seasons and hydrologic conditions.

Water quality at the major water supply intakes in the Delta is a public health concern. Six such stations are monitored routinely. They include:

- (1) American River Water Treatment Plant intake that serves the City of Sacramento (station 1 AMERICAN);
- (2) North Bay Pumping Plant (station 87 BARKERNOBAY) near Dixon that serves Solano and Napa Counties;
- (3) Rock Slough at Old River (station 9 ROCKSL), which is 4 miles east of the Contra Costa Water District (CCWD) intake;
- (4) Contra Costa Water District Pump Station 1 (station CONCOSPP1) at Oakley;
- (5) Harvey O. Banks Delta Pumping Plant Headworks (station 12 BANKS), which is the headworks of the State Water Project (SWP); and
- (6) DMC intake at Lindemann Road (station 11 DMC), which is upstream of the Tracy Pumping Plant for the Delta-Mendota Canal (DMC).

Water quality monitoring stations that were sampled during 1991 are listed in Table 2.2. The assigned program station number, official DWR station code, location, abbreviated station name, and station type, drainage (AD) or nondrainage (HF), are shown.

Most channel or export facility monitoring stations are sampled each month. Drainage stations are sampled during periods of major farming activity that could increase drainage volume and affect drain water quality (e.g., summer irrigation and winter field leaching months). The age and condition of the drainage pump stations vary (Photos 2.1 and 2.2). Some channel stations were sampled twice each month in the southwestern Delta to study bromide distribution resulting from from sea water intrusion and entrainment. At least four times per year, synoptic surveys are conducted to collect data on the geographic distribution of channel water quality changes measured within a few hours. The channel stations within the Delta are shown in Figure 2.1. Drain water collection sites are shown in Figure 2.2.

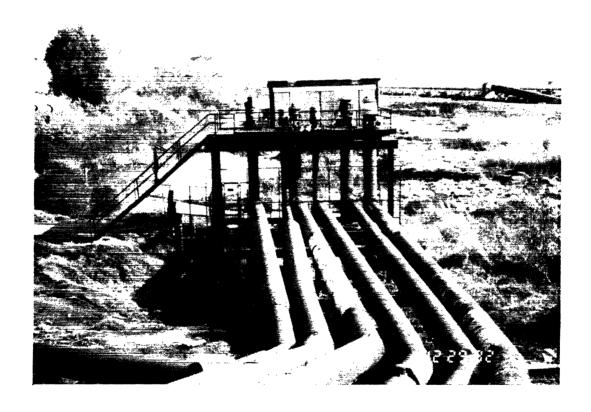


Photo 2.1. Upper Jones Tract pump station An example of some of the older pump station structures that are still in operation in the Delta.

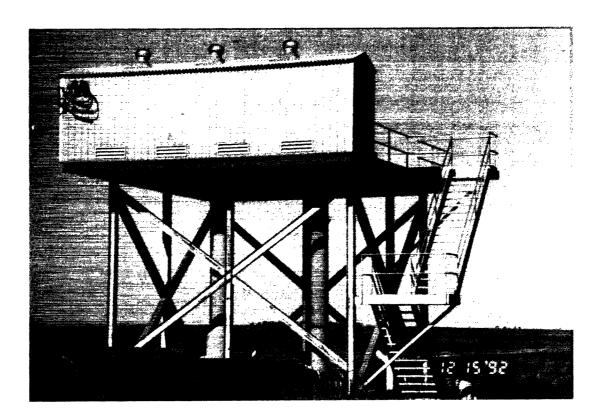


Photo 2.2. Staten Island pump station. One of the newer drainage pump stations in the Delta.

Table 2.2. Monitoring Stations

PROGR	AM DWR	•		
STATION	STATION COD	E STATION LOCATION	STATION NAME	TYPE
1	A0714010	American River at Water Treatment Plant	AMERICAN	HF
2	B9D82071327	Sacramento River at Greene's Landing	GREENES	$_{ m HF}$
5	B9V81171369	Ag Drain on Grand Island	AGDGRAND	AD
7	B9D80371300	Little Connection Sl. @ Empire Tract	LCONNECT	$_{ m HF}$
8	B9V80361299	Ag Drain on Empire Tract, W.end 8-Mi. Rd.	AGDEMPIRE	AD
9	B9D75841348	Rock Slough @ Old River	ROCKSL	HF
10	KA000000	Clifton Court Intake	CLIFTON	$_{ m HF}$
11	B9C74901336	DMC Intake @ Lindemann Rd.	DMC	HF
12	KA000331	Delta P.P. Headworks	BANKS	HF
13	B9D75351293	Middle R. @ Borden Hwy.	MIDDLER	$_{ m HF}$
14	B0702000	San Joaquin R. nr. Vernalis	VERNALIS	$_{ m HF}$
17	E0B80261551	Sacramento River @ Mallard Island	MALLARDIS	$_{ m HF}$
20	A0V83681312	Natomas Main Drain	NATOMAS	AD
	B9V80541310	Ag Drain on Bouldin Tract, PP. No. 1	BOULDIN1	AD
	B9V80611335	Ag Drain on Bouldin Tract, PP. No. 2	BOULDIN2	AD
25	B9V80461224	Ag Drain on King Island, PP. No. 1	KINGISPP01	AD
26	B9V80271262	Ag Drain on King Island, PP. No. 2	KINGISPP02	AD
27	B9V80331273	Ag Drain on King Island, PP. No. 3	KINGISPP03	AD
	B9V74811246	Ag Drain on Pescadero Tr., PP. No. 1	PESCADERO01	AD
	B9V74811241	Ag Drain on Pescadero Tr., PP. No. 2	PESCADERO02	AD
46	B9V74821231	Ag Drain on Pescadero Tr., PP. No. 3	PESCADERO03	AD
	B9V81801307	Ag Drain on Pierson Tr., PP. No. 1	PIERSONPP01	AD
50	B9V80001255	Ag Drain on Rindge Tract, PP. No. 1	RINDGEPP01	AD

Table 2.2. (cont.). Monitoring Stations

PROGRAM DWR			
STATION STATION COD	E STATION LOCATION	STATION NAME	TYPE
51 B9V80271282	Ag Drain on Rindge Tract, PP. NO. 2	RINDGEPP02	AD
59 B9V75441298	Ag Drain on Upper Jones Tr., PP. No. 1	UPJONESPP01	AD
60 B9V75641318	Ag Drain on Upper Jones Tr., PP. No. 2	UPJONESPP02	AD
61 B9V80671368	Ag Drain on Brannan Island, PP. No. 1	BRANNANPP01	AD
62 B9V80711377	Ag Drain on Brannan Island, PP. No. 2	BRANNANPP02	AD
63 B9V80721385	Ag Drain on Brannan Island, PP. No. 3	BRANNANPP03	AD
64 B9V80741398	Ag Drain on Brannan Island, PP. No. 4	BRANNANPP04	AD
65 B9V74961340	Ag Drain on Clifton Court	AGDCLIFTON	AD
68 B9V74781220	Ag Drain on Pescadero Tract, PP. No. 4	PESCADERO04	AD
69 B9V74661251	Ag Drain on Pescadero Tract, PP. No. 5	PESCADERO05	AD
75 B0704000	San Joaquin R. @ Maze Rd. Bridge	MAZE	$_{ m HF}$
80 KA007089	CA Aqueduct, Ck 13, O'Neill Outlet	CHECK 13	$_{ m HF}$
87 B9D81661478	Barker Sl @ North Bay PP	BARKERNOBAY	HF
88 B9D80961411	Sacramento River @ Rio Vista Bridge	SACRRIOVISTA	HF
91 B9D80361275	Honker Cut at Atherton Road Bridge	HONKER	$_{ m HF}$
100 B9D75891348	Old R. N/O Rock Sl (St 4b)	STATION04B	HF
103 B9D75351342	Old R. nr. Byron (St 9)	STATION09	HF
105 B9D74971331	West Canal at Clifton Court FB Intake	WSTCANCLIFT	HF
107 B9D81481305	Delta Cross Channel Gate nr Walnut Grove	DELTACRCHAN	HF
108 B9D81441309	Georgiana Slough at Walnut Grovelxridge	GEORGSLWALNUT	HF
110 B9D75741317	Middle River at Bacon Island Bridge	MRIVBACON	HF
111 B9D75011229	Middle River at Mowry Bridge (Undine Rd)	MIDMOWRY	HF
112 B9D75881285	Turner Cut at McDonald Island Ferry	TURNERCUT	HF
113 B9D80191348	Old River at Sand Mound Slough	SANDMOUND	HF
114 B9D80011307	Middle River nr Latham Sl (Ferry Site)	LATHAM	HF
115 B9D80031294	Connection Sl. at Mandeville Isl Bridge	CONNMAND	HF
117 B9D75651333	Santa Fe-Bacon Island Cut nr Old River	SANTAFEBACON	HF
118 B9D75481334	Woodward/N. Victoria Canal nr Old River	NVICWOOD	HF
119 B9D75171329	North Canal nr Old River	NORTHCAN	HF
121 B9D74931328	Grant Line/Fabian/Bell Canals nr Old R.	GRANTOLD	HF
122 B9D74891331	Old River U/S from DMC Intake	OLDRIVDMC	HF
123 B9V80451387 124 B9V80381361	Ag Drain on Webb Tract, PP. No. 1	WEBB01 WEBB02	AD AD
125 B9V75931350	Ag Drain on Webb Tract, PP. No. 2 Ag Drain on Holland Tract, PP. No. 1		AD AD
	Ag Drain on Holland Tract, PP. No. 2	HOLLANDO1	AD
126 B9V80011348 127 B9V80111361	Ag Drain on Holland Tract, PP. No. 3	HOLLANDO2 HOLLANDO3	AD AD
128 B9V75881342	Ag Drain on Bacon Island, PP. No. 1	BACON01	AD AD
129 B9V80031328	Ag Drain on Bacon Island, PP. No. 2	BACON02	AD
130 B9D80311413	San Joaquin River at Jersey Point	SJRJERSEY	HF
131 B9D80301377	False River at Southerly Tip of Webb Tr.	FALSETIP-WEBB	HF
132 B9D74951331	Old River 6/10 mile below DMC intake.	OLDR-DMC-CLIFT	
133 B9D7584XXXX	Contra Costa Pumping Plant @ Rock Slough	CONCOSPP1	HF
411 B9D80771345	Mokelumne R. below Georgiana Sl	MOKGEORGIANA	HF
413 B9D80691298	L. Potato Slough @ Terminous	LPOTTERM	HF
602 B9D74711184	San Joaquin R. @ Mossdale Bridge	SJRMOSSDALE	HF
604 B9D74731285	Old River nr Tracy	OLDRTRACY	HF
605 B9D75291273	Middle R @ Tracy Rd Bdq	MRIVTRACY	HF
606 B9D74921269	Grant Ln Can @ Tracy Rd Bdg	GRANTLNCAN	HF
000 200, 000	wit out o not body		

Type Code:

AD refers to agricultural drain.

 ${
m HF}$ refers to nondrainage station. H code referred to Interagency Health Aspects Monitoring Program station and ${
m F}$ for freshwater sample type.

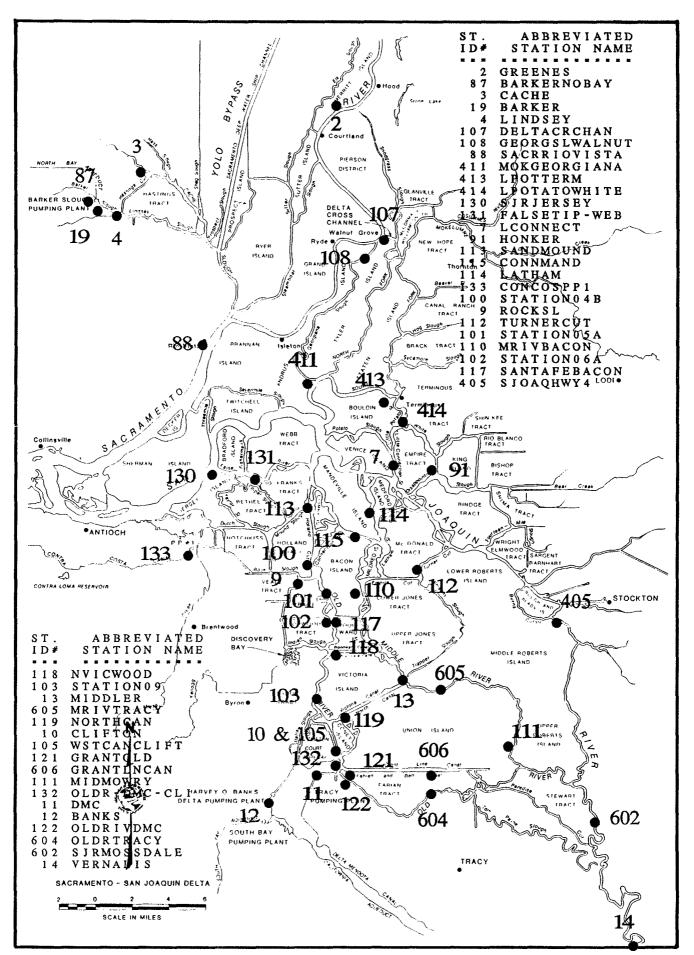


Figure 2.1. Channel Stations

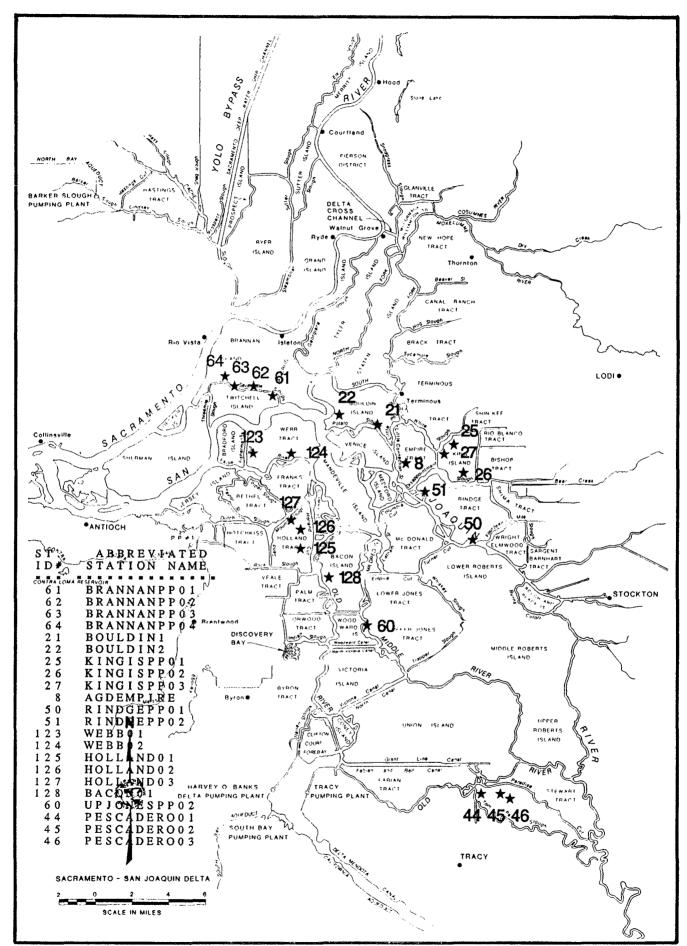


Figure 2.2. Agricultural Drain Sampling Sites

Methodology

Field

Two-person teams are assigned on rotation to specific sampling runs. Each run requires sampling at about ten sites in the Delta (about 250 miles roundtrip). Two converted full-size vans serve as mobile field laboratories for on-site field measurements and the filtering of water samples. A 21-foot inboard/outboard cabin cruiser is used for sampling in open-water areas.

All equipment, vans, and the boat are stored at the DWR Bryte Yard facility, where DWR's water testing laboratory is also located. A 55-foot trailer and storage shed serve as the program's Monitoring Support and Logistics Center (Photo 2.3).

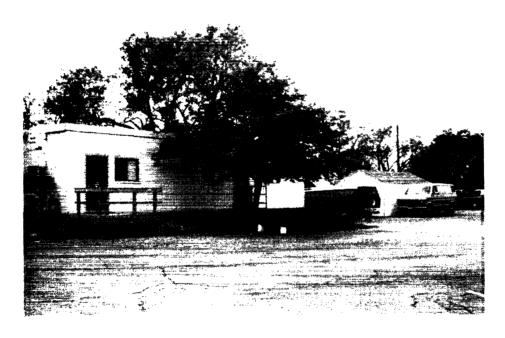


Photo 2.3. MWQI Monitoring Support and Logistics Center. MWQI's center for field sampling equipment, storage, and preparation.

Field instruments are checked and calibrated prior to each run. Field data entry forms and laboratory sample submittal forms are computer generated and placed into separate binders with maps and additional instructions for each field team. The forms indicate sampling stations, sample bottle series, keys for entry, and other special handling requests. All teams are in radio communications with each other for emergencies and last-minute changes to the sampling runs.

Drainage samples are collected from platform structures (e.g., trash rack, pump station walkway) or culverts. Channel water samples are collected by boat or from structures (e.g., gauge station, bridges, docks, and piers; Photo 2.4).



Depending on analytes, the water samples are collected using either a plastic pail, stainless steel bucket, or a stainless steel boxshaped bucket designed by DWR. The latter is fitted with two Teflon® coated spigots to fill bottles for on-site field measurements such as dissolved oxygen, pH, or electrical conductivity. Before the samplers are used, they are washed with Alcojet® detergent and heat dried in an automatic dishwasher. The bucket is rinsed out with new sample water at each site to prevent carryover from the previous sample.

Photo 2.4. Sampling the Delta. Field operations leader Mike Sutliff collecting water sample from Greenes Landing station on the Sacramento River.

A Yellow Springs Instrument® (YSI) electrical conductivity/temperature meter is used to record the sample EC and temperature. A Beckman® model 10 portable pH meter is used to determine pH with a Hellige® colorimetric pH kit serving as a backup unit. The pH meter is calibrated to two buffered pH standards (pH 4 and 10). Dissolved oxygen is measured with a Yellow Springs Instrument® model 50A or 50B dissolved oxygen (DO) meter. Saturated air calibration is used to set the DO meter after a 10-minute warm-up. The other electrical meters are calibrated before use on each data collection run and left on for at least 30 minutes to stabilize prior to taking measurements. DO samples are collected in an Erlenmeyer flask with a Teflon® coated magnetic stir bar placed inside. The DO probe is inserted into the flask and a magnetic stirrer mixes the sample.

A stainless steel filtering apparatus with a 0.45 micron porosity paper filter is used to filter samples. A peristaltic pump with surgical grade silicone tubing is used to transfer the sample through the filter. Demineralized water and fresh sample water are used, respectively, for wetting the paper filter onto the filter support screen and for flushing out the tube lines to eliminate carryover from the previous sample.

Filtered samples for THM and DOC (dissolved organic carbon) measurements are collected in 40 ml. glass vials (Photo 2.5). THM vials are filled to eliminate air space and bubbles.



The caps of the 40 ml. vials are fitted with Teflon® coated septa, as specified by the U.S. Environmental Protection Agency (EPA). Samples are kept on ice, or refrigerated and delivered to the laboratory within 24 hours of collection. (Note: As of July 1992, samples for THM analyses are collected into 250 ml. bottles.)

Photo 2.5. Mobile laboratory. Field crew member Walt Lambert filtering water samples for DOC and THMFP analyses in one of the program's mobile laboratories.

A filtered water sample is collected for bromide and UVA-254 (ultraviolet absorbance at wavelength 254 nm) measurements by the laboratory. Additional filtered samples are collected

for selenium and some cation (e.g., Ca, Mg, Na, K) analyses and are fixed with nitric acid. Ultra pure nitric acid vials are used. Unfiltered samples are collected for color and turbidity readings by the lab.

In March 1991 staff began to measure turbidity in the field with a Hach® 2100P portable turbidimeter that is calibrated against reference turbidity standards. However, laboratory turbidity values appear in the database as the official measured turbidity, because the Hach 2100P has not yet been tested for use as an EPA approved instrument that meets the EPA methodology. The Hach® 2100P readings are consistently higher than the laboratory values because of a different optical path.

All sample bottles are stored in large ice chests with ice packs until delivered to the laboratories.

On occasion, staff collect additional volumes of water for the Metropolitan Water District of Southern California (MWDSC) for testing and experimentation. These samples are shipped to MWDSC in ice chests via overnight express delivery on the day of collection. Results of these studies are not reported by the MWQI Program but are available from MWDSC.

Field duplicates are collected on each sampling run (usually one sample in seven to ten samples). The duplicates are submitted as "blind samples" to the laboratories with the regular samples as a quality assurance check. Field blank samples are run when metals or nutrient analyses are requested.

Field measurements are recorded on field data sheets and lab sample submittal forms. All equipment is returned to the field preparation center for cleanup, maintenance, and preparation for the next sampling run. Batteries are replaced or recharged, and demineralized water tanks are refilled. Vans are restocked with acid vials, filter paper, disposable gloves, and other expendable items. The vans and boat are serviced regularly according to a maintenance schedule or whenever problems arise.

All members of the study team, including consultants, participate in the sampling runs. This ensures that sampling schedules are maintained and that the team members know and understand all facets of the study. Currently, field quality assurance procedures that are followed are those specified in DWR's Sampling Manual for Environmental Projects, April 1994.

Laboratory

The total THM formation potential (TTHMFP) assay was developed by DWR to compare different water types found in the Delta. At the receiving laboratory, water samples for TTHMFP analysis are chlorinated (inoculated) with about 120 mg/L chlorine with sodium hypochlorite. This high dosage is used to assure a chlorine residual after the seven-day incubation period at 25 degrees Celsius. At the end of seven days, the chlorine residual is determined. The residual chlorine is then quenched using sodium thiosulfate, and the sample is analyzed for THM by gas chromatograph purge and trap methodology in EPA Methods 501, 502.2, or 601. During the five-year period, THM analyses were performed by three commercial laboratories. Clayton Environmental Consultants (Pleasanton) performed analyses from January 1987 to June 1987; Enseco Laboratories (West Sacramento) performed analyses from July 1986 to June 1989; and PACE Laboratories (Santa Rosa) performed analyses from July 1989 to June 1992. The three laboratories were instructed to follow the aforementioned procedure for THMFP analyses.

Bromide analyses of samples taken after November 14, 1990 were performed by DWR's Bryte Laboratory. Prior to that date, bromide analyses were performed by Enseco Laboratories (Colorado facility). Enseco results were slightly higher than the Department's laboratory results because of different analytical methodologies.

From 1987-91, DWR's Bryte Laboratory performed mineral, bromide, and DOC analyses by following EPA Method 600-4-79-020, Methods for Chemical Analysis of Water and Wastes (Revised March, 1983) and the U.S. Geological Survey's Methods for Determination of Inorganic Substances in Water and Fluvial Sediments. Further detail about laboratory methods used by Bryte Laboratory may be found in DWR's The Delta As A Source of Drinking Water, Monitoring Results 1983-1987. Some of the DWR laboratory methods are shown in Table 2.3.

The Department's laboratory staff currently follow the latest EPA-approved methods and in-house developed laboratory quality assurance and quality control procedures.

Table 2.3. DWR Laboratory Methods

Constituent	Method	Reporting limit *
Calcium	EPA 215.1 AA Flame	1 mg/L
Magnesium	EPA 242.1 AA Flame	1 mg/L
Sodium	EPA 273.1 AA Flame	1 mg/L
Potassium	EPA 258.1 AA Flame	0.1 mg/L
Sulfate	EPA 375.2 Colorimetric, MTB, Automated	1 mg/L
Chloride	EPA 325.2 Colorimetric, Ferricyanide, Automated	1 mg/L
Nitrate	EPA 353.2 Colorimetric, Cd-Reduction, Automated	d 0.1 mg/L
Dissolved Solids	EPA 160.1 Gravimetric, 180° C	1 mg/L
Alkalinity	EPA 310.1 Titrimetric	1 mg/L
рН	EPA 150.1 Electrometric	0.1 pH Unit
Specific Conductance	EPA 120.1 Wheatstone Bridge	1 μmhos/cm
Turbidity	EPA 180.1 Nephelometric (Hach)	1 NTU
Trihalomethane (THM)	EPA 502.2 Purge and Trap, Gas	l μg/L
Potential	Chromatography (GC)	
Color	EPA 110.2 Colorimetric, Pt-Co	5 Color Units
Organic Carbon	EPA 415.1 Wet Oxidation, IR, Automated	0.1 mg/L

Methods used at DWR Chemical Laboratory (Bryte Lab) in West Sacramento.

<u>Note</u>: The above analytical methods were approved EPA methods during 1987-91. Since that time, the Department's laboratory staff use the current EPA-approved methods.

^{*} Reporting limit for reagent water

Data Management

Field measurement and laboratory results are entered into the program's Local Data System Interface (LDSI) database as data sheets are received. The LDSI database software program was written to offer a variety of management and support services for the MWQI Program. Some of the major features include: (1) sample bottle numbering, labelling, and tracking, (2) field data sheet form generation, (3) simplified data entry handling, (4) report generation, (5) selection of duplicate sample locations, and (6) data transfer capabilities with other computer software formats (e.g., databases, spreadsheets).

The LDSI software program was written in-house using the MicroRim R:base for DOS 2.11 command language. Data entry errors are checked visually and by running computer searches for anomalous data (e.g., negative or zero values, statistical outliers). The accuracy of typing the database entries generally exceeds 99 percent.

Data are transferred from the LDSI Reporter database format for analysis and interpretation. Depending on specific data needs and objectives, the data are transformed and transferred into other formats acceptable by a variety of statistical and graphical computer software. Flow data from DWR's DAYFLOW model or State Water Project Operations and Maintenance records might also be merged with the water quality data. Technical support and data analysis are provided under contract by the water quality/computer consulting firm of Marvin Jung & Associates, Inc. in Sacramento. This consulting firm also provides additional services for DWR's Delta Modeling Section, which is refining a Delta THMFP computer model.

Laboratory Quality Control

Laboratory quality assurance procedures are in accordance with the DWR Bryte Chemical Laboratory Quality Assurance Program document dated April 4, 1990. DWR staff developed an Interim Project Quality Assurance Plan to ensure data integrity in the MWQI Program. The interim plan was based on guidelines developed by EPA for EPA projects. Questions concerning data quality are routed to the program staff for review and action. The Quality Assurance Program unit is alerted about potential field and laboratory instrumentation and analytical problems. Based on the chain of custody records, field logbook data sheets, and laboratory quality control reports, staff identifies problems and the proper course of action to resolve them.

Chapter 3. STATE OF KNOWLEDGE

This chapter summarizes important issues regarding THM formation, new regulations on disinfection by-products, precursors in Delta water supplies, and current knowledge about precursor sources.

Meeting Standards

Water utilities are required to meet federal and State drinking water standards that have been established for the protection of human health. These standards include a variety of chemical, physical, and microbiological requirements.

Chemical disinfection is necessary to prevent bacterial growth and taste and odor problems in a water supply distribution system. Chlorination is a highly reliable and economical method of disinfection and is widely used by water utilities including those that use the Delta as a water source. During the chlorination process, chlorine reacts with certain complex organic compounds and bromide ions in the water to form disinfection by-product compounds including trihalomethanes (THMs). One THM, chloroform, is classified as a carcinogen. The total THM levels in drinking water are regulated by the State and federal governments.

The THMs include four compounds: chloroform (CHCl₃), dichlorobromomethane (CHCl₂Br), dibromochloromethane (CHClBr₂), and bromoform (CHBr₃). Currently, the Maximum Contaminant Level (MCL) for total THMs is 0.100 mg/L (equivalent to 100 µg/L or parts per billion) in treated water samples as a running annual average of quarterly samples taken from representative points in a drinking water distribution system. The MCL was not established strictly on the basis of health effects data but was set as a feasible level for compliance by water utilities. However, under stage 1 of the new Disinfectants-Disinfection By-products (D-DBP) rule, the EPA will lower the MCLs for THMs to 0.080 mg/L in June 1998.

The production of THMs and several other disinfection by-products can be generally shown as:

When free chlorine or other oxidants are added to water, the above reactions occur. Natural organic matter such as decaying algae, soils, sewage wastes, and organisms provide the carbon source to react with chlorine. If bromide is not present, only chloroform will be formed as the chlorine reacts with the natural organic precursors. Bromide, another precursor, can exacerbate the problem of meeting the 0.100 mg/L THM MCL and new 0.080 mg/L THM MCL because the heavier THM compounds containing bromine atoms, will be formed. Chlorine oxidizes bromide to hypobromous acid (HOBr), which then reacts with the organic precursors to form the brominated methanes.

THMs are not the only compounds of health concern these days. EPA is expanding its list of chemicals for regulation. New MCLs will cover oxidants and by-products of the oxidants (Trussell, 1992) and disinfectants. EPA is resolving the debate over the regulation of these chemicals through a negotiated regulatory process (Means and Krasner, 1993). Particular emphasis is focused on the technical uncertainties that complicate the setting of health-protective Maximum Contaminant Levels for several disinfectants and their by-products.

Several other problems in water treatment are associated with the presence of high concentrations of organic matter. Some of them include color, taste and odor, reduced longevity of activated carbon beds, and possible transport of organic and inorganic pollutants through the treatment plant and into the finished water supply (Dempsey, et. al., 1984).

As of March 1994, stage 1 of the D-DBP rule includes a 0.80 mg/L TTHM MCL, a 0.60 mg/L MCL for the total sum of five specified haloacetic acids (HAA5), a 1.0 mg/L MCL for chlorite, a 0.010 mg/L MCL for bromate, and disinfectant limits. Stage 1 limits will come into effect in June 1998. Stage 2 limits may further reduce the TTHM MCL to 0.040 mg/L and the HAA5 to 0.030 mg/L in January 2002.

Water utilities are researching new treatment technologies to meet the anticipated new EPA drinking water standards. However, if precursors to these toxic compounds could be reduced in the source water, then treatment requirements may be lessened. For example, high levels of organic matter in source water require higher amounts of oxidant. This, in turn, results in higher concentrations of DBPs that must be removed. Removal of these by-products are more difficult and more expensive. Improving source water quality combined with improved treatment technologies could help utilities meet the new EPA MCLs.

Bromide and organic matter have been identified as the major precursors that must be controlled. Stage 1 of the D-DBP rule will also require reducing the total organic carbon (TOC) concentration in water supplies prior to adding disinfectant. TOC measurements are used as a surrogate measurement for organic DBP precursors. The stage 1 precursor removal requirement will apply only to conventional water treatment plants (coagulation, flocculation, sedimentation, and filtration) and to softening plants. It will not apply to systems using direct filtration, slow sand filters, diatomaceous earth filters, or ground water supplies not under the direct influence of surface water.

TOC removal will be based on the source water alkalinity. A specified percentage of the TOC in the source water will need to be removed prior to adding disinfectant. For example, the following table shows that if the source water quality had a TOC of 5 mg/L and an alkalinity of 40 mg/L, at least a 45 percent reduction in TOC is required. With some exceptions and depending on season and location, Delta TOC is typically 2 to 6 mg/L and alkalinity 40 to 120 mg/L. Enhanced coagulation or softening will be the likely practice used.

		Source Water Alkalinity, mg/L	
Source water TOC, mg/L	0 - 60	> 60 - 120	> 120 *
> or = 2 - 4	40 %	30 %	20 %
> 4 - 8	45 %	35 %	25 %
> 8	50%	40 %	30 %

^{*} Systems practicing softening must meet TOC removal requirements in this column.

DWR began routine monitoring of the THMFP of Delta water supplies in 1983 under the Interagency Delta Health Aspects Monitoring Program. The purpose was to understand the sources and distribution of THM precursors in the Delta. DWR developed a raw water supply THMFP test to compare the relative THMFP of different water types in the Delta. These water types included sea water, brackish water, fresh water, and agricultural drainage. The results, however, cannot be used to simulate finished drinking water TTHMFP in a distribution system because of different oxidant dosages, treatment practices, and technologies used in treating drinking water.

THMFP can serve as a surrogate for the formation potential of some other DBPs, although sometimes a reduction of THMs by some water treatment processes may increase the concentrations of other DBPs. Therefore, water agencies are deeply concerned about the formation of THMs and other DBP compounds that challenge their ability to provide a safe drinking water supply, especially now that new and stricter standards are forthcoming.

THM Precursors and Sources

The study of trihalomethane precursors and their sources is important for determining how trihalomethane formation might be controlled. Trihalomethane precursors can be divided into two classes: organic and inorganic. Humic materials are an example of the organic type and bromide is the inorganic type found in drinking water supplies. In the Delta, the sources of these precursors differ.

Bromides

Bromides are of concern because formation of DBPs increases in the presence of bromides. Also THMs that contain bromine weigh more than chloroform, thereby increasing the likelihood of violating the current and proposed MCLs for total trihalomethanes in finished drinking water. Brominated methanes are also generally more difficult to control and remove than chloroform using current treatment processes. In addition, bromides react with some disinfectants to form other undesirable DBPs. A reduction in bromide concentrations in a water supply would help water treatment plants in meeting the new D-DBP rule and reduce some additional treatment requirements.

The Delta has three sources of bromide. One major source is sea water that enters the western Delta from tidal excursions and mixes with Sacramento River water flowing through the Delta to the export facilities in the southern Delta. Bromides in water at Clifton Court Forebay and at the Contra Costa Water District intake are attributed to sea water intrusion. Another source of bromide is the San Joaquin River (SJR). Bromide may have naturally occurring sources in the San Joaquin Valley, but the primary source probably is from agricultural return water which contains bromide and is exported from the Delta. Monitoring of Br:Cl ratios, flow measurements, and selenium concentrations (DWR, 1990) in the lower Delta demonstrated this connection. Another source is connate water beneath some islands (e.g., Empire Tract).

Organic Precursors

Natural organic matter (NOM) has many origins in the Delta. Sources may include organic soils and sediments, algal growth, riparian and crop vegetation, animal wastes, waste water discharges, and river inflows to the Delta.

Soils with greater carbon content, such as peat, introduce higher concentrations of DOC and THM precursors into drainage water than do mineral soils. Composited peat soil samples had 67,000 ug/kg THMFP, while composited mineral soils had 27,000 ug/kg THMFP (DWR, 1982). The ranges of THMFP in drain water corresponded to soil types or organic content as seen in August and January drain water samples (DWR, 1990).

Living crop biomass is not thought to be a significant contributor of THMFP relative to island soils. However, crop residues such as stalks and leaves are a source of humus as this material dies and decays. The decomposing crop residue is relatively small in volume and depth (inches) compared to the underlying peat soil depth (several feet). Therefore, carbon in the underlying soil is the expected major contributor of DOC and TFPC.

Evidence shows that submergence of organic soils causes higher DOC concentrations in the drain water, because microbial decomposition and dissolution of decomposing organic matter are enhanced (Deverel, pers. comm., 1991).

A variety of complex substances is present in naturally occurring dissolved organic carbon. These substances can be classified into four major groups: (1) identifiable compounds, (2) hydrophilic acids, (3) humic acid, and (4) fulvic acid. The latter two are collectively referred to as humic substances and are known THM precursors (Oliver and Thurman, 1983; Rook, 1974).

There are differences in the types and reactivities of DOM substances in Delta drainage and channel water samples. Drainage samples are more reactive than channel water samples because of high amounts of humic substances. They had four times more THMFP and ten or more times more DBPs than Delta river samples (Amy and others, 1990). This is in agreement with MWQI THMFP data. Structurally, humic materials in drain water have larger molecules and weight than river water, so the type of humics in DOC is as important as the amount. These observations also indicate that the drain water humics are from the soils and decaying crop residues. They are not from river water or from applied water, nor from concentrating effects of

evapotranspiration or evaporation of irrigation water.

The yield of trihalomethanes in Iowa River water samples as a function of precursor molecular weight was studied by Schnoor (Schnoor and others, 1979). Most THMs formed from precursors of molecular weight less than 6000. Seventy-five percent of the THMs formed were derived from organics of less than molecular weight 3000 and about 20 percent from compounds of less than molecular weight 1000. This latter fraction has been cited to include fulvic acid compounds. Differences in THM yield per TOC (weight to weight basis) were attributed to the precursor molecular weight distribution among samples.

Reckhow and Singer (1984) compared the organic halide yields from extracted humic materials. For all organic halides, humic acid had higher yields than fulvic acid from the same water source. The percent distribution of TOX (total organic halides) was surprisingly uniform. Seventy percent of the TOX was chloroform, 18 percent was TCAA (trichloroacetic acid), and 6 percent was DCAA (dichloroacetic acid) in a three-day reaction time chlorination test.

Other studies (Thurman, 1985) show that the composition of DOC varies in different aquatic environments. The total amount of humic and fulvic acids in DOC is about 50 percent in rivers, 75 percent in wetlands, 30 percent in lakes, 25 percent in ground water, and 20 percent in sea water (Figure 3.1).

Currently, the contribution of organic matter and THM precursors from phytoplankton and riparian plants in the channels has not been assessed. The effluents of waste water treatment plants may not be a major source of THM precursors (DWR, 1982).

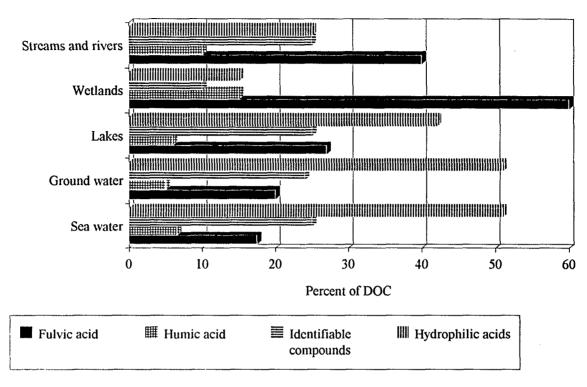


Figure 3.1. Composition of DOC. Figure modified from Thurman and others, 1985

Soil and Aquatic Humus Formation

An understanding of the origin and the processes of humus formation is important for assessing potential impacts from a variety of proposed activities in the Delta. These include creating wetlands, storing water in reservoirs, and dredging and widening channels.

When fields are leached, a variety of factors can change the composition and character of the drain water constituents. There are changes in dissolved oxygen, pH, microbial populations, and the types of inorganic and organic matter. Interstitial water from reduced environments (anaerobic) are flushed into open ditches (aerobic environment) with thriving microbial populations. Further decay and transformation of the organic material will occur with rates that vary with seasonal environmental conditions. The chemical behavior (e.g., solubility, contribution to water electrical conductivity) of mineral salts in an organically rich, acidic medium is also changed.

Aquatic humic substances originate from soil humic material and terrestrial and aquatic plants (Thurman and others, 1985). Delta soils and, therefore, drainage water are naturally enriched in humic and fulvic acids from decomposing matter. Because of the underlying decaying organic soils, Delta islands are major storage pools of soil humic substances. Drain and river waters will mostly have aquatic humics.

Soil and aquatic humus differ. Stevenson (1982) proposed four pathways for the formation of humus in soil. The theories revolved around lignin and/or cellulose degradation from plant material. Cellulose content can be up to six times more than the lignin content on a percentage weight basis.

A proposed composite hypothesis is that aquatic humic substances are the result of several processes in the aquatic environment (Thurman, 1985). The type of water and time of year are major factors in the origin of humic substances in water. The processes or origins include:

- (1) Leaching of plant organic matter into the surrounding water;
- (2) Chemical and biochemical alteration of plant material as it is leached through the soil;
- (3) Leaching of both soil fulvic and humic acids into the water;
- (4) Lysis of algal remains and bacterial degradation of phytoplankton;
- (5) Photo-oxidation of organic matter at the surface; and
- (6) Polymerization of biological products in water.

Thurman and Malcolm (1983) found that input from land (processes 1 to 3) are more important for streams and rivers. Processes 4 and 5 may be more important in lakes and oceans (Harvey and others, 1983). In the autumn when leaves fall and are leached by autumn rains, processes 1 and 2 are important (Caine, 1982). In case of low stream flow, ground water is a major input and soil and sediment interstitial waters may be most important (Thurman, 1985). For the Delta, processes 1 through 4 and interstitial waters from soils are probably important sources of humic substances in the drainages at certain times of the year.

Except for ground waters and wetlands, the oxidative process rather than polymerization is dominant on fulvic and humic acids in water. However, in reductive environments, such as water-logged soils, ground waters, and interstitial waters, the large concentration of organic

matter and preservation of phenolic groups enhances the opportunity for polymerization of humic substances (Thurman, 1985). In fresh plant extracts, bacteria enzymatically cleave the natural plant products, which are high in carbohydrate, and increase the carboxyl content. Phenols are oxidized to quinones and undergo polymerization reactions. Therefore, the subsurface Delta island soils, which by nature are water saturated, organically enriched, and in a reducing environment, will probably continue to be a vast generator of humic substances.

The impact of ponding Delta islands for water storage or using them as a waterfowl habitat with respect to DOC and THMFP concentrations in the stored water is uncertain. Supporters of wetland and water storage projects on Delta islands argue that the deep inundation of the islands will inhibit oxidation of organic soils and, thereby, reduce the availability of DOC and loading of THM precursors. USGS studies indicate that DOC will still be available regardless of the oxidative state because of the abundant supply of soluble organic matter on the islands (Deverel, pers. comm.). A pilot study may be the only method to determine the effects of using an island to store water.

Drainage Volume

About 1,000 siphons and 260 drainage pump stations are on nearly 60 islands and tracts. Most of the pump stations have more than one discharge pipe. Drainage discharge data are essential for estimating the loadings and impacts of DOC and THMFP precursors from drainage. The most complete study of Delta drainage volumes was conducted nearly 40 years ago in 1954-55 and published in DWR Report No. 4 (DWR, 1956). Historical Delta land use records show significant changes in the crops grown during the last 40 years. Asparagus was the dominant crop in the 1950s and 60s. Corn is now the major crop. It is not known if these crop changes have affected drainage volume because of different water demands and farming practices.

DWR and the USGS are conducting a joint study to measure and estimate the applied and drainage water volumes in the Delta. Power consumption data and measured flows will be used. Program staff members are obtaining permission from landowners and the reclamation districts to install these temporary devices at pump stations and siphons. The joint study began in December 1993. The monitoring equipment will be rotated to different islands to compare new computed estimates to those in DWR Report No. 4. Until these estimates are updated, DWR Report No. 4 provides the best data of Delta-wide drainage volume by region and month. The 1954-55

drainage volume estimates are discussed in the section titled "Drainage Discharges" in this report.

Behavior of DOC

Understanding the behavior of DOC compounds is important for following their fate and transport in the Delta. Saunders (1976) proposed the following generalization about the decomposition rates of dissolved organic matter (DOM). Simple low molecular weight organic compounds decompose most quickly with turnover times of less than one hour to several hours. Higher molecular weight organics released by phytoplankton and bacteria decompose in 2 to 10 days. Other higher molecular weight dissolved organics decompose on the order of 100 days, and another class of organics that takes longer than 100 days to decay probably exists. This suggests that the highly reactive humic substances, or THM precursors in island drainages originating from the organic soils, will be more persistent than humics in water applied to the islands. In fact, humic substances, the most reactive fraction of the DOM in forming THMs, are very resistant to degradation. Carbon dating has established that humics in the Suwanee River in Florida are 30 years old. The nonhumic fraction of the DOM, consisting largely of biochemicals such as proteins and amino acids, is more biodegradable (G. Amy, pers. comm., 1990).

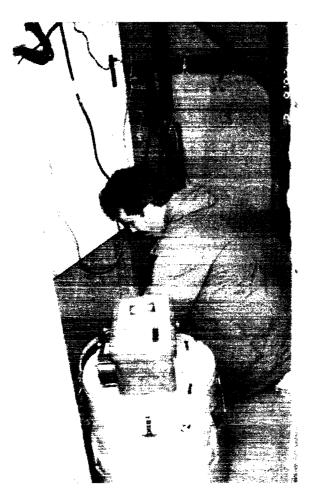
The relationship between salinity and DOC in an estuary has been studied by many. Salinity, reported in parts per thousand, is defined as the total solids in water after all carbonates have been converted to oxides, all bromide and iodide have been replaced by chloride, and all organic substances have been oxidized. Salinity is numerically smaller than total dissolved solids (APHA, 1981). Some studies have found a conservative behavior of DOC in estuaries such as the North Dawes, Beaulieu, Ems, Rhine, and Severn (Loder and Hood, 1972; Moore and others, 1979; Laane, 1982; Eisma and others, 1982; Mantoura and Woodward, 1983).

Mantoura and Woodward (1983) found that degradation did not significantly change the DOC concentration during its 200 day residence time in the Severn Estuary. Other studies showed that precipitation and flocculation of DOC, particularly humic substances, occurred at salinities of 5 parts per thousand and more (Sholkovitz, 1976). Sholkovitz (1976) found only I percent to 6 percent, removal of DOC in the Amazon estuary by precipitation. However, the humic acid, which accounted for 5 percent to 10 percent of the DOC was nearly all removed in the estuary (60 percent to 80 percent). It appeared that fulvic acid was not removed in the Amazon estuary.

Aquatic fulvic acids generally have molecular weights of less than 2,000 and are more soluble than humic acids which have molecular weights from 2,000 to 5,000 or more. Humic acids are more colloidal in size and will, therefore, "salt out" in saline estuarine waters.

While these studies show different conservative behavior in an estuary, they agree that in waters of less than 5 parts per thousand salinity (<5,000 mg/L), DOC behaves conservatively.

The conclusion based on the above studies is that estuarine waters of 5 parts per thousand or more salinity will tend to remove by precipitation the more reactive THM precursor humic acid fractions in DOC carried downstream by river inflow.



The studies show that humic substances (fulvic and humic acids) in Delta waters may be treated as conservative constituents because of short water residence time relative to decay rates and low salinities. With the exception of a few Delta sloughs, water flowing into the Delta is generally transported to the export pumps or out into the Bay in a few days or weeks. This assumption has also been used in the Department's Delta modeling studies.

Photo 2.6. Automated water sampler. New automated sampling devices are being installed at six sites for studying daily and sometimes hourly changes in DOC and other water quality parameters in the channels and drains.

Chapter 4. RESULTS

The objective of the five-year data analysis was to summarize current knowledge about the sources and distribution of organic carbon in the Delta. Although not all drains have been monitored nor drainage volume estimates updated, in some cases, sufficient data exists to make educated guesses about unsampled drainages and the overall impact of organic matter from them on Delta channel quality.

The following results and topics are presented in this chapter:

Regional and Seasonal Patterns.

This section summarizes information on the differences in soil types, DOC, humics, and drainage volume across the Delta and with season. This information is useful in identifying major sources and activities that affect DOC distribution in the Delta. The data serves as a framework for developing a computer model on regional and seasonal changes in Delta THMFP.

Drainage Organic Carbon Releases.

Estimates on the amount of organic carbon from island drainage and in-channel sources are presented. A simple model, based on current data and reasonable assumptions, was used to conceptualize DOC input to the Delta and to identify additional monitoring needs.

♦ Modified THMFPC Assay.

Improvements to the DWR THMFP assay for Delta waters are described. The new method eliminated previous underestimates of THM formation potential of high DOC water samples (more than 20 mg/L). The old method yielded lower THMFP results for some drain water samples but not for nondrain water samples.

♦ Surrogate Measurements.

This section describes correlations among UVA, DOC, and TFPC. The relationships were useful in identifying and explaining some of the underestimated THMFP concentrations caused by the old DWR THMFP assay. The relationships of UVA to DOC, called specific absorbance, may also serve as a tracer for the source and age of organic matter in Delta soils. Future telemetered monitoring systems might include in-situ UVA measurements if the relationships and accuracy are acceptable. If the UVA to TFPC and UVA to DOC

relations are useful, earlier data where DOC was measured could be used to estimate past UVA. From the estimated UVA, past underestimated THMFP data or TFPC data could be corrected. In any case, the study of surrogate measurements may improve modeling input data.

Other Water Quality Concerns.

Selenium and sodium monitoring results are summarized.

♦ Data Quality Review.

Results of an evaluation of the integrity and operations of the program's quality assurance and quality control protocol are summarized with recommended actions.

Regional and Seasonal Patterns

Significant progress has been made in understanding the distribution and nature of THM precursors in the Sacramento-San Joaquin Delta. Much of the observations about drainage water quality are predictable and are associated with the prevalent soil characteristics of the surrounding area. The regional and seasonal patterns of DOC, TFPC, and other indicators of precursor availability are discussed in the following sections.

Soils

The natural history of the Delta explains the tremendous supply of organic matter in the region. Much of the area was once a vast tule marsh. Reclamation activities over the last 100 years have removed this vegetation for farming. The deep layers of peat, over 30 feet thick in some areas, came from the decay of marsh plants (the great bulrush or tule, *Scirpus lacustris*).

Delta soils are grouped into three simple classes: mineral, intermediate organic, and peaty organic. Mineral soils have the least amount (less than 10 percent) of organic matter and peaty organic the most (about 50 percent to 80 percent). Organic soils are confined to the Delta basin and occupy about 250,000 acres. Mineral soils are located along the margins of the basin. The organic soils in the basin are more typical of the low-lying area and the mineral soils represent a transition zone where basin organic soils begin to mix with upland mineral soils that originate from areas beyond the Delta boundaries. The regional soil types in the Delta are shown in Figure 4.1.

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As time passed there was a constant layering of soil and a mixture of partially and fully decomposed organic matter. Soil horizons of older and younger material were created and can be seen in deep soil profiles (Thurman, 1985).

Most of the central Delta has soils classified as Staten and Venice peaty muck that have 60 percent to 70 percent organic matter. Most areas with intermediate organic type soils (Ryde silty clay loam) has 30 percent to 50 percent organic matter.

Previously, it was found that TTHMFP concentrations in island drainage are associated with the soil type (DWR, 1990). Drainage from peaty organic regions had the highest THMFP concentrations, and mineral soil areas had the least amount during the peak summer and winter months of drainage discharge. Other water quality parameters were found to be associated with soil type and are discussed in the following sections.

Dissolved Organic Carbon (DOC)

<u>Drains.</u> The organically enriched Delta peat soils on Bouldin Island have high porosity with compaction less than 10 percent vol/vol (Deverel et al., 1986). This is probably typical of most peat areas. Deep crevices extend from the surface to a few feet (Deverel, pers. comm., 1991). The soil's low compactness results in innumerable macro and microchannels throughout the soil column. These channels serve as conduits for water movement across and vertically through the loose spongy peat soil. They also allow soil contact with air, which leads to oxidation. Studies conducted for DWR by the U.S. Geological Survey have measured over 90 percent carbon loss as carbon dioxide on Twitchell Island. This carbon loss is attributed to microbial decay and surface oxidation (Deverel, pers. comm., 1991). Most subsidence or loss of soil in the Delta is attributed to natural oxidation processes occurring in the soils.

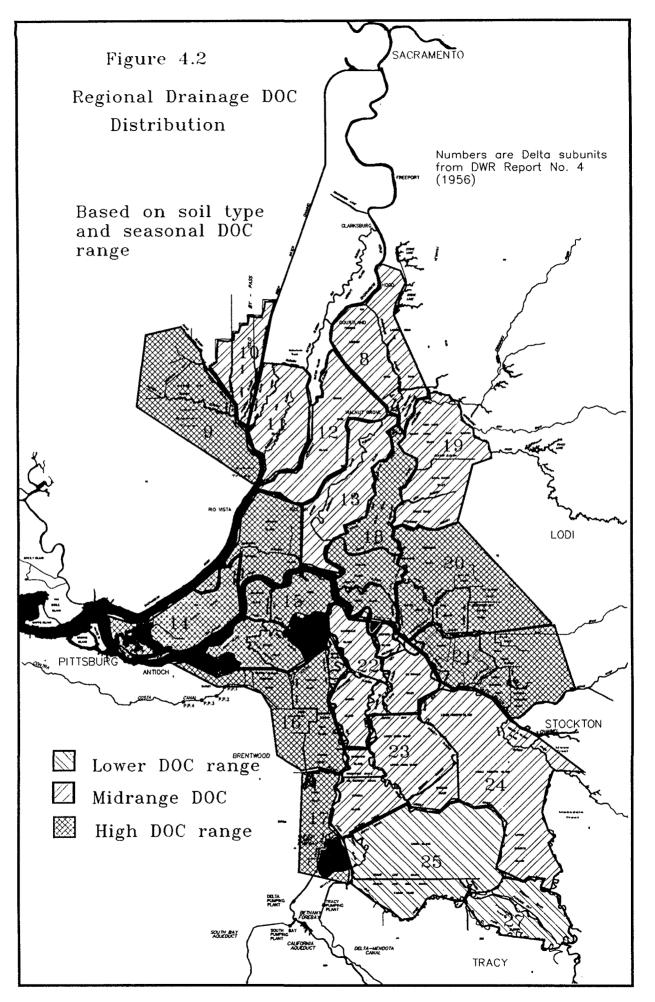
Organic matter is carried away as water passes through these soils from irrigation, rainfall, flooding, seepage, and leaching. Due to head, hydraulic gradients, and capillary action, interstitial water in the porous peat soil is displaced as new water enters the soil. New water enters from spud ditches that provide subsurface irrigation to crops during the growing season. In winter, water is applied (i.e., ponded or flooded) to fields for salt leaching. The water eventually empties into the drainage canals and is generally high in salts and organic matter.

There are regional and seasonal differences in the ranges of DOC concentration in Delta drainages. The regional pattern was most evident when drainage DOC concentrations of subunits of the Delta were compared by wet (October to April) and dry (May to September) seasons. These subunits are groups of islands and tracts (DWR, 1956). The subunits could be grouped into three distinct subgroups to describe the regional DOC concentrations. Figure 4.2 shows the predicted regional pattern of DOC which correlates with soil type. Some island drainages are not sampled so the predicted regional patterns are based on observations of adjacent areas.

The monthly DOC concentrations for all sampled drains are shown in the box-and-whisker plot in Figure 4.3. The maximum, upper quartile (75 percent), average (indicated by "+" within the box figures), and median values are indicated in the figure. Overall the average values were higher than the median values and represented a 60 to 80 percentile value depending on month. The average, median, and upper quartile values were closest to each other during May through October, a period when DOC is least variable. The highest DOC concentrations as seen by average and 75 percentile values occur in December to March. The monthly data show a lognormal distribution as seen by the positions of the median and 75 percentile values in relation to the total range of values.

During late fall and early winter, the farmers siphon water onto the fields to remove salt. Berms are created by the farmers to create a small wall (1-2 feet high) around the fields to facilitate ponding. As water enters the island from the siphons around the islands, the drainage pumps are temporarily shut off to allow the fields to quickly fill. The drainage pumps resume operating after the fields are flooded. The hydraulic head and operation of the drainage pumps, respectively, push and pull water through the soil beneath the ponded fields. The highest DOC concentrations in drainage typically occur during this period and are attributed to the dissolution of organic matter in the fields and underlying soil. During these months, DOC levels in the drainage may increase by two to three times higher than in the drier months.

Lower DOC concentrations, sometimes seen in November through February, might have reflected conditions prior to when the fields were flooded or after drainage from the flooded fields was pumped off the islands.



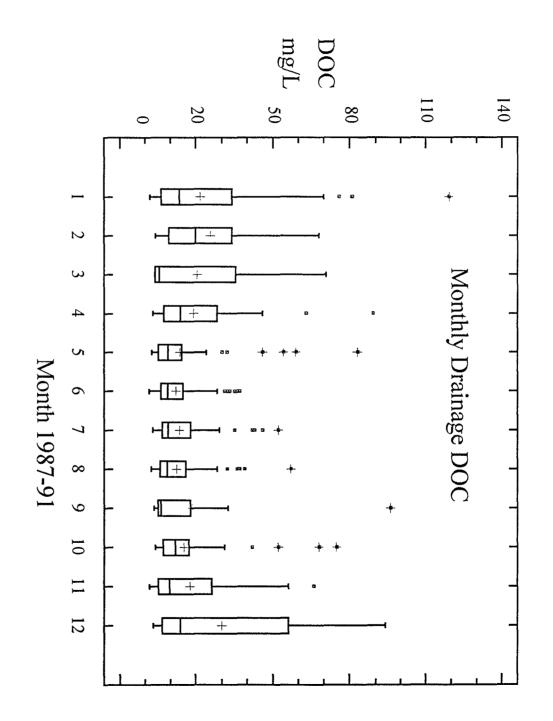


Figure 4.3. Monthly DOC at Sampled Delta Drain Pump Stations

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The wide range of DOC concentrations within a group of islands or at a drainage station for the same month could be explained by the following:

- 1. Not all fields were farmed that year. For example, in the summer of 1991, the State instituted a Drought Water Bank, whereby farmers were compensated for water not used for crop production during the drought. About 40 percent of the Delta lands were fallowed under this program.
- 2. There are changes in the irrigation schedule and amount due to changing crop needs. Some crops and stages of a crop have different watering needs. Some areas may be harvested earlier than others.
- 3. Seepage water from adjacent channels is the predominant water source collecting in the drainage. This might be the case if fields were not farmed.
- 4. Most of the "available" soluble organic matter had already been removed from the winter ponding of fields. Organic matter would again be available with time as environmental conditions (e.g., warmer temperatures, oxidation, and microbial activity), which favor organic decay, are reestabished. With time, DOC levels in interstitial waters would increase.
- 5. There are regional differences in soluble organic matter in a drained field. Some islands have more than one soil type so the drainage water quality at each pump station may differ significantly.
- 6. Microbial degradation has caused a loss of DOC in the drains. DOC is converted to carbon dioxide gas and released into the atmosphere. The rate of degradation is expected to be higher during the warm months than in the cool months, because temperature has a positive effect on microbial activities (e.g., population growth, metabolism).
- 7. The contact time of water with soil organics is short, so leaching is incomplete. The water table fluctuates with season, and a lower elevation results in less soil moisture and contact time.

The monthly range of DOC values for each of the three Delta subgroups is shown in

Figure 4.4. The seasonal high and low DOC months are similar for the high and intermediate level DOC drainages. Seasonality is less distinguishable for the low DOC region where mineral soils are found because of limited sampling during February to May.

The difference between wet and dry month DOC levels may represent the impact of flooding the fields to remove salt during the winter. A study to achieve salt reduction with less applied water could mutually benefit the reclamation districts, power utility provider, and downstream water users. Less applied water would result in less drainage being pumped off the islands. This, in turn, would result in lower electrical costs and reduced wear of pumps for the reclamation districts. The power utility company would also benefit from postponing the need for building new power facilities to meet future growth. Downstream users would benefit if DOC pumped into the channels could be reduced.

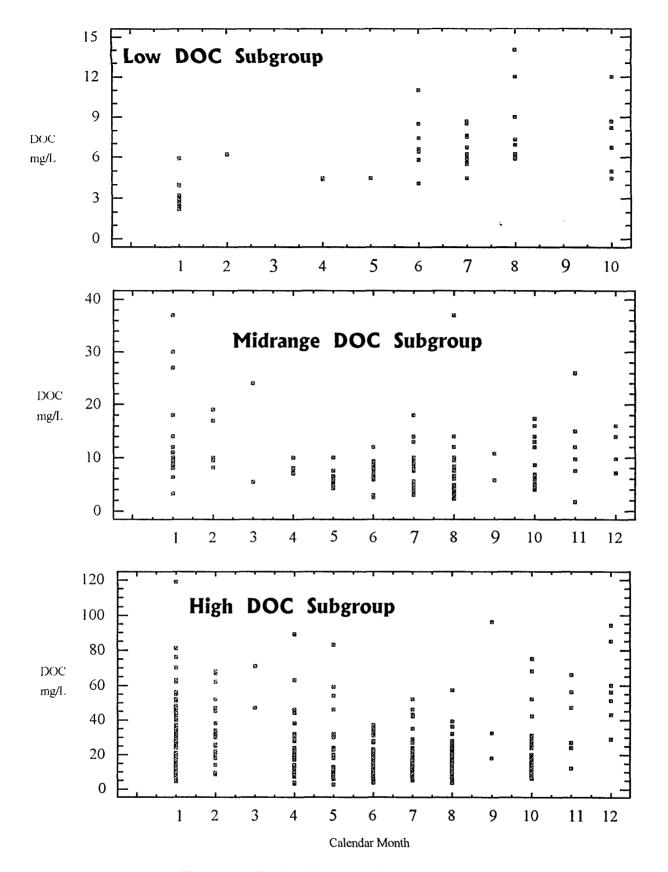


Figure 4.4. Regional Monthly Drainage DOC

Channels. Monthly DOC in the Delta channels did not show a definitive increase due to successive dry years. The highest DOC concentrations coincided with periods when fields were flooded and drained in the winter (December to February), storms occurred (March 1991), and fall rice field drainage was released upstream of the Delta on the Sacramento River (September). Winter DOC concentrations are 2 to 3 mg/L higher than during the summer months. The monthly DOC at eight Delta stations is shown in Figures 4.5 to 4.7 for calendar years 1987-91. DOC data for some stations prior to 1988 were not available, as TOC was measured instead of DOC. TOC is equal to or higher than DOC concentrations and varies with time and sampling location. There is no constant relationship between these two measurements.

The DOC data are important in view of recent proposed EPA regulations on allowable TOC concentrations in raw water supplies prior to disinfection. By 1997, enhanced coagulation will be necessary for most, if not all, users of Delta waters to meet the Surface Water Treatment Rule. For waters with TOC ranging from 2 to 4 mg/L, 30 percent of the TOC must be removed before applying chlorination. For waters with 4 to 8 mg/L TOC, 35 percent of the TOC must be removed. All systems with more than 2 mg/L TOC must do pilot studies to evaluate GAC and membrane filtration during the next few years for the second round of negotiated regulations with EPA in 1998 (Krasner, pers. comm. 1993).

The plots show that even waters from the American River and Sacramento River at Greenes Landing will, on occassion, have TOC above 2 mg/L based on DOC data. DOC concentrations at major water diversion sites (e.g., Banks headworks, DMC intake) often exceed 4 mg/L and during storm events reach 8 mg/L. Delta drainage and storms can cause the DOC to double in concentration. DOC is expected to increase in the channels during normal and wet year conditions. New federal drinking water standards may result in DOC control which may, to some extent, override concerns for THMFP of State water supplies.

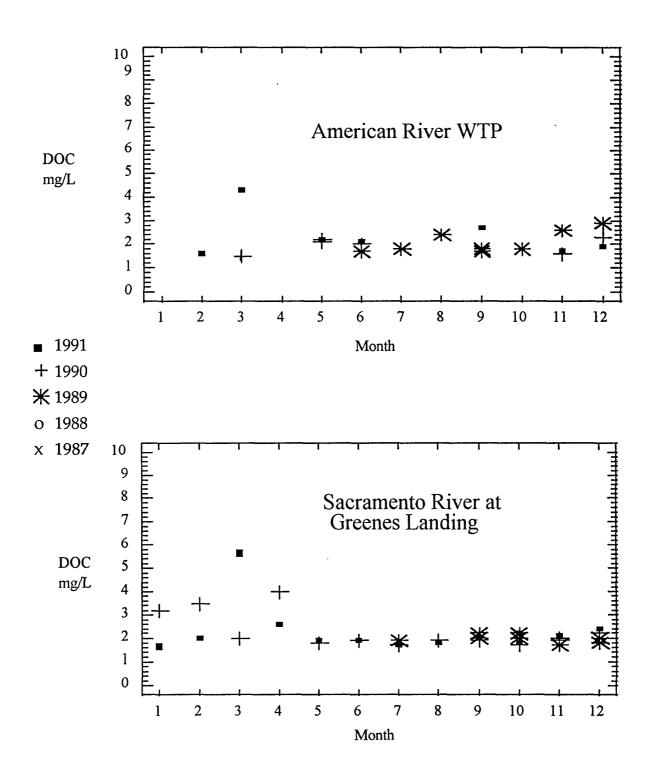


Figure 4.5. Monthly DOC at Upper Delta Stations

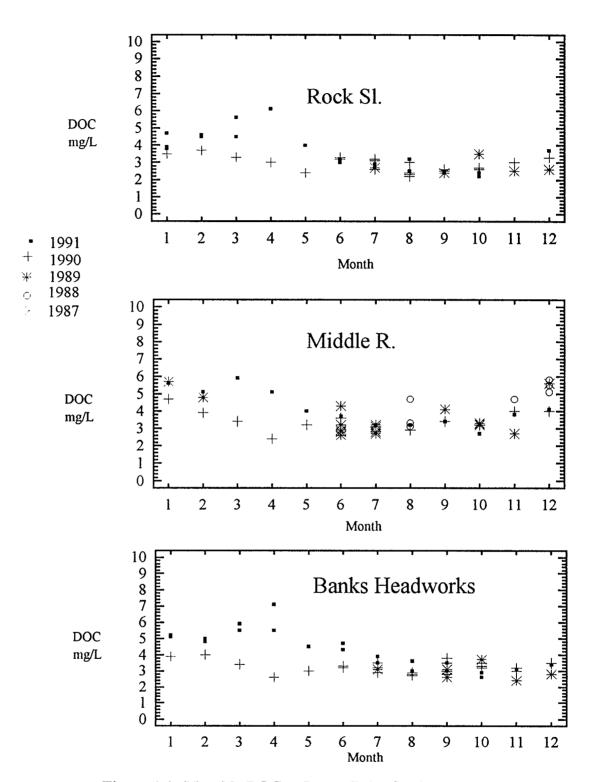


Figure 4.6. Monthly DOC at Lower Delta Stations

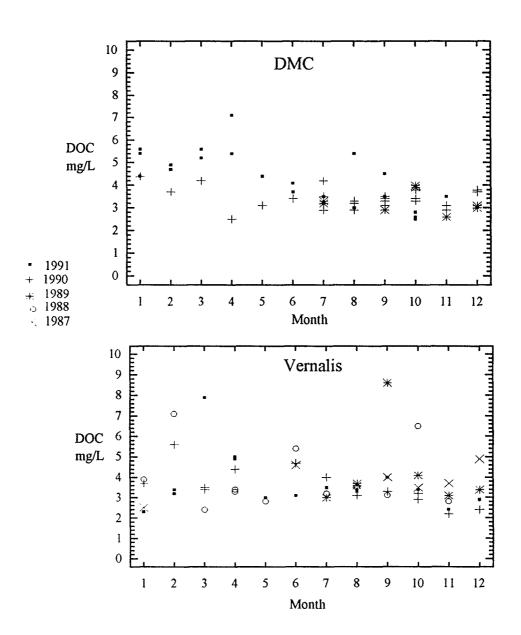


Figure 4.7. Monthly DOC at DMC intake and Vernalis Stations

Island DOC Loads

A computation was made for the estimated mass loads of DOC applied onto an island and removed by pumping drainage. For comparison, the calculations were made for a southern Delta mineral tract, Pescadero, and for an intermediate organic soil island, Grand Island. July data were used because according to DWR Report No. 4: Quantity and Quality of Water Applied To and Drained from the Delta Lowlands (DWR, 1956), July received about one-third of the total water during the irrigation season (March - October). There were no applied water data for November to February to calculate mass load for these months. To simplify the estimates, the following data were used:

- 1. The July 1954-55 data on applied water and drainage water volumes for those two areas were used as no recent data were available.
- 2. The approximate average July DOC concentrations for each island based on the MWQI monitoring program were used.
- 3. It was assumed that water applied to Grand Island could be represented by Sacramento River at Greenes Landing water quality data and that water applied to Pescadero Tract could be represented by data from the San Joaquin River near Vernalis.

The example calculations showed:

- 1. Grand Island drainage had one-third to nearly one-half more DOC in total pounds than in the applied water. This is attributed to the high organic content of the island's soil and drainage volume.
- 2. In contrast, the mass amount of DOC discharged from Pescadero Tract was significantly less (reduced by 74 to 80 percent) than that amount applied onto the island. This is attributed to the low organic content of the soil and lower drainage volume at Pescadero.
- 3. The ratios of the volumes of applied water to drainage water were significantly different between the two islands. The ratios at Grand Island

ranged from 2.7:1 to 3:1 and at Pescadero Tract from 6.6:1 to 8:6:1. These differences are likely linked to soil type differences and crop demands.

Summary of Example Calculation

	Grand Island	Pescadero Tract
General soil class	organic	mineral
Applied water volume /1	10,655 AF	8,150 AF
Applied water DOC	2 mg/L	3.5 mg/L
concentration /2	(Greenes Landing)	(Vernalis)
Applied water mass load	57,921 lbs.	77,531 lbs.
DOC		
Drainage water volume /1	3560 AF (1954);	1231 AF (1954);
	3927 AF (1955)	948 AF (1955)
Drainage DOCconcentration	8 mg/L	6 mg/L
/2		
Mass load DOC	77,409 lbs.;	20,075 lbs.;
pumped out	85,389 lbs.	15,460 lbs.
Mass In minus Out	19,488 lbs;	(57,456 lbs.);
	27,468 lbs.	(62,071 lbs.)
Percent gain or (loss)	33.6 % and 47.4 %	(74 %) and (80 %)
Ratio of applied to drainage	3:1 and 2.7:1	6.6:1 and 8.6:1
volume		

^{1.} Applied (July 1954) and drainage water (July 1954 and July 1955) volumes from DWR Report No. 4: Quantity and Quality of Water Applied To and Drained from the Delta Lowlands, July 1956.

Similar patterns are expected for other islands and tracts of similar soil classification. These results, although illustrative and based on old applied and drainage volume data, concur with and further support the conclusions previously stated regarding how important regional soil type, organic content, and drainage volume affect the availability and release of DOC from the islands.

To update information on current conditions, the Department and the U.S. Geological Survey have launched a joint study of Delta water use. This study will measure the volumes of applied and drain water on several islands beginning with Twitchell Island. Water quality will also be monitored to compute mass loads of constituents. The results of this study will be used to update consumptive use estimates for the Delta.

DWR MWQI DOC data for Sacramento River at Greenes Landing, agricultural drain at Grand Island, San Joaquin River near Vernalis, and agricultural drains at Pescadero Tract.

Humics

<u>Drains</u>. Natural dissolved organic matter has the physical characteristic of absorbing ultraviolet light at different wave lengths. Measurements of that characteristic at the ultraviolet (UV) wave length of 254 nm is a standard laboratory procedure.

The predominant UV absorbing organic material in natural waters is humic material. Humic and fulvic acids in wetlands constitute about 75 percent of the DOC. Humic acid absorbs ultraviolet light more than fulvic acid but is generally four to five times lower in concentration (Thurman, 1985). Pure humic acid and fulvic acid produce 11.7 and 7.6 millimoles of chloroform per mole of chlorine consumed, respectively (Babcock and Singer, 1979). Moist conditions of swampy areas may promote the formation of the smaller molecular weight humic substances (fulvic acids) by interfering with molecular condensation reactions (Gjessing, 1976). These reactions are a key step in forming the macromolecules that comprise the humic acid fraction. This might explain why there is more fulvic acid than humic acid in wetland areas such as the Delta.

Specific absorbance is the ratio of the ultraviolet absorbance (UVA) per cm at 254 nm to the DOC concentration (mg/L). Drainage samples generally had specific absorbance within three ranges:

Range 1: Low-range 0.0 to less than 0.03

Range 2: Mid-range 0.03 to less than 0.06

Range 3: High-range 0.06 and above but generally less than 0.20

The specific absorbance of drain water probably indicates different stages and amount of humification (humics vs. nonhumics and types of humics remaining) in the soils. Lower specific absorbance is expected from areas with fresh organic matter or less mature or less available humic material. As microbial decay progresses, the ratio increases and becomes more stable over time as DOC is reduced and released as carbon dioxide into the atmosphere. The remaining UV absorbing organics are the biorefractory humics. The proportion of UVA compounds might also shift.

The significance of these specific absorbance ranges is that they, in combination with other water quality measurements, could be used to track the impact of drainage on regional water

quality in the channels as well as explain the regional differences in observed THMFP or TFPC.

The ratios correlated with the regional soil type of the sampled drain (Figure 4.8). In general, the mineral soil areas had the low-range ratios. Peat areas had mid-range ratios, and areas with mixed soil types had more than one range. Drain samples with mid-range specific absorbance have higher TFPC than the low and high specific absorbance samples. This suggests that the mid-range group of organics is rich in THM precursor compounds. For simple comparison, the drainage data were grouped by location into areas. These areas corresponded to Delta units studied in the Department's 1954-55 drainage water quantity and quality study (DWR, 1956). Some areas had multiple ranges of specific absorbance. Delta Unit 15 (Brannan and Twitchell islands) had values in the three ranges. The soils of these two islands are intermediate organic in character. Unit 16 (Holland, Palm, and Orwood tracts) had specific absorbance in the middle and high ranges. Holland Tract soils are classified as peat and those of Palm and Orwood are intermediate organic. The drain at Clifton Court Forebay in Unit 17 (Clifton Court and Byron Tract) had ratios mostly in the mid-range, but some samples were in the low-range. These multiple ranges might reflect the mixed soil types (mineral and intermediate organic) along the southwestern border of the Delta lowlands.

Some Delta units had stable specific absorbance in the middle range. These were Unit 18 (Staten and Bouldin islands), Unit 20 (Empire and Terminous tracts and King Island), Unit 22 (Bacon, McDonald, and Mandeville islands), and Unit 23 (Lower and Upper Jones tracts). The soils of these areas are organic peat. Drain water from Pescadero Tract, which represented Delta Unit 27, had low specific absorbance but was high in bromides. The low specific absorbance probably reflects the low humic content of the mineral soil in this region.

In summary, drainage from Delta mineral soil areas had low specific absorbances of less than 0.03. Drainage from peat areas had ratios in the 0.03 to less than 0.06 range. Areas of intermediate organic soils had drainage with multiple ranges of specific absorbances. These ratios are indicators of the distribution of humic organic matter.

<u>Channels</u>. MWQI channel stations were grouped into subregional water quality characteristics (e.g., EC) and put into channel zones for this analysis (Table 4.1). The channels had distinct ranges of specific absorbances that corresponded to the primary water sources and drainage quality of that region (Figure 4.9).

The specific absorbances were low at the American River station and at the downstream North Lowland stations (channel zones 1 and 2). This area lies north of the San Joaquin River that extends out to the western Delta and north of Potato and White sloughs. Both low and midrange specific absorbances were observed in channel zones (i.e., zones 3, 4, 5, and 6) southward of this region. However, stations along Middle River in channel zone 6 had more mid-range values than low values. Specific absorbance of drainage from the central Delta peat areas are predominantly mid-range and are the likely cause of the mid-range values in the channels. South Delta stations (channel zone 7) had low values as did the San Joaquin River stations at Maze Road and Vernalis.

The specific absorbance of Sacramento River at Mallard Island samples varied, with about two-thirds of the observed values in the mid-range and the remainder in the low-range. Western Delta stations in channel zone 5 and at the Banks headworks also had about the same proportion of mid-range to low-range ratios as the Mallard Island station had. However, the specific absorbances at the DMC intake were about evenly distributed between low- and mid-range values. The difference in the distribution of specific absorbance at the Banks headworks and DMC intake may be due to differences in the operation of these two facilities. The DMC operates continuously while the Banks facilities has gates at Clifton Court Forebay to regulate the intake of water during tidal periods and varying seasonal water needs.

In general, the specific absorbances are low in the northern Lowlands region and San Joaquin River stations. The western and central Delta regions had both low- and mid-range values. The regional channel specific absorbances do appear, in part, to correspond to local drainage specific absorbances. These comparisons could be used to assess the impact of local drainage discharges on channel water quality.

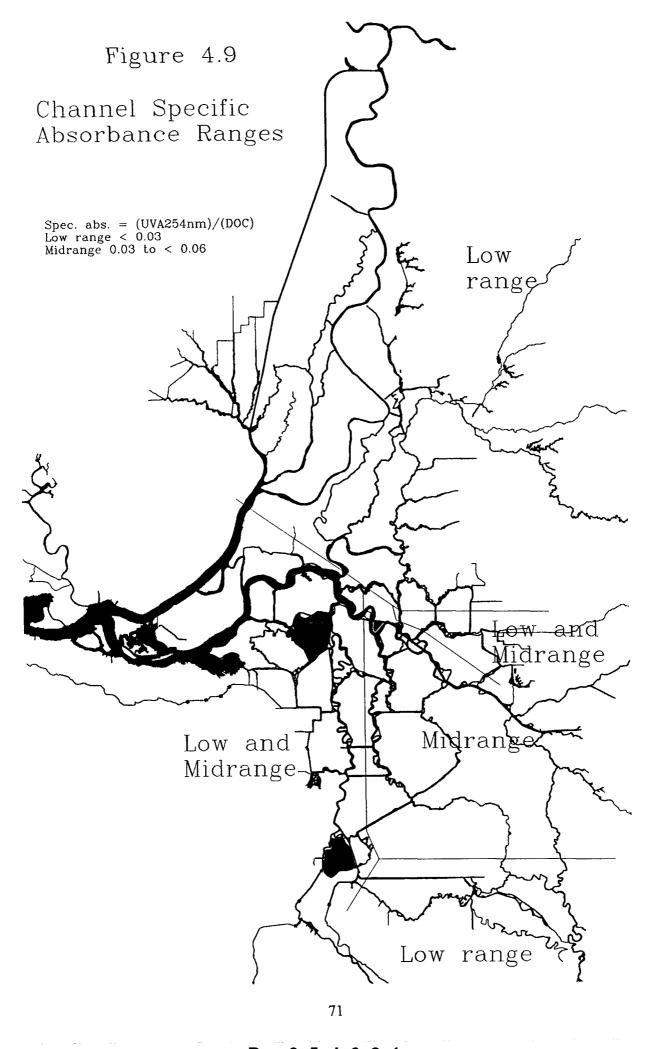
The use of UVA to estimate DOC concentrations and the importance of specific absorbance for predicting TFPC are both discussed in "Surrogate Measurements."

Table 4.1. Channel Zones

Channel Zone	Station No.	Station Name
1	2	Sacramento River at Greene's Landing (GREENES)
North	107	Delta Cross Channel (DELTACRCHAN)
Lowlands "A"	108	Georgiana Sl. at Walnut Grove
2	411	Mokelumne River at Georgiana Sl. (MOKGEORGIANA)
North	413	Little Potato Sl. at Terminous (LPOTTERM)
Lowlands "B"	414	Little Potato SI. at White SI. (LPOTATOWHITE)
3	88	Sacramento River at Rio Vista (SACRIOVISTA)
4	91	Honker Cut (HONKER)
North	7	Little Connection Sl. (LCONNECT)
Central Lowlands		
5	131	False River at Webb Tract (FALSETIP-WEB)
Western Lowlands	113	Old River at Sandmound Sl. (SANDMOUND)
	130	San Joaquin River at Jersey Pt. (SJRJERSEY)
	100	Station 4B at Old River (STN04B)
	9	Rock Sl. at Old River (ROCKSL)
	101	Station 5A at Old River (STN05A)
	102	Station 6A at Old River (STN06A)
	103	Station 9 at Old River (STN09)
	121	Grant Line/Fabian/Bell Canal at Old River (GRANTOLD)
	122	Old River upstream of DMC intake (OLDRIVDMC)
6	112	Turner Cut (TURNERCUT)
South Central	114	Latham Sl. (LATHAM)
Lowlands	115	Connection Sl. at Mandeville Isl. (CONNMAND)
	110	Middle River at Bacon Isl. (MRIVBACON)
	117	Santa Fe-Bacon Isl. Cut near Old River (SANTAFEBACON)
	118	Woodward/N. Victoria Canal near Old River (NVICWOOD)
	13	Middle River at Bacon Isl. (MIDDLER)
	119	North Canal near Old River (NORTHCAN)
	405	San Joaquin River at Highway 4 (SJOAQHWY4)

Table 4.1. (cont.). Channel Zone List

Channel Zone	Statio	n No.	Station Name
7	606	Grant Line Canal	at Tracy Road bridge (GRANTLNCAN)
South Delta	604	Old River at Trac	y Road (OLDRTRACY)
Lowlands	111	Middle River at N	Nowry bridge (MIDMOWRY)
	602	San Joaquin Rive	r at Mossdale bridge (SJRMOSSDALE)
8 Northwest Delta	87	North Bay Pumpi	ng Plant (BARKERNOBAY)
Delta Boundary and Intake Station	ns		
	I	American River a	it Water Treatment Plant (AMERICAN)
	2	Sacramento River	at Greene's Landing (GREENES)
	17	Sacramento River	at Mallard Isl. (MALLARDIS)
	14	San Joaquin Rive	r near Vernalis (VERNALIS)
	75	San Joaquin Rive	r at Maze Rd. (MAZE)
	133	Contra Costa Wa	ter District Pumping Plant # 1 (CONCOSPP1)
	12	H. O. Banks Head	lworks (BANKS)
	11	DMC intake at Li	indemann Rd. (DMC)



Drainage Discharges

Through past reclamation work, the Delta was subdivided into more than 60 islands and tracts for crop production, each complete with its own reclamation district with levees, drainage, and irrigation facilities. In general, past irrigation and drainage practices continue today.

Most water for irrigation is from adjacent stream channels through a pipe siphon, which arches upward to a point just below the crest of the levee. Irrigation water is generally carried in ditches about 10 feet wide that run parallel to the levee about 100 feet inside the inner toe and discharge into lateral ditches 4 feet wide. These lateral ditches dissect the island into checks ranging from 20 to 50 acres. Water flowing from these laterals enter smaller, temporary spud ditches, about 10 inches wide and about 20 inches deep. These spud ditches parallel the crop rows at every 50 to 100 feet.

Water is controlled to the desired height by dams in the lateral ditches and baffles in the spud ditches, causing the water level to rise in each check. The ground water is maintained at different levels for different crops and stages of growth.

Excess water from the spud ditches discharges into ditches that carry the water to the next check. This excess eventually empties into drainage canals about 10 feet deep and 25 feet wide. These canals carry the drainage to the pumping plant. The pumping plant lifts the drainage over or through the levee and discharges it back into the stream channel outside the levee. Automatic float switches operate the large electric pumps at each pump station. Multiple discharge pipes and pumps are common at a pump station. Most of the islands require more than one pump station to remove drainage from the entire island.

The most comprehensive study of drainage volume discharges in the Delta was conducted nearly 40 years ago in 1954-55 (DWR, 1956). Monthly estimates of discharge volume were based on electrical power consumption records and pump efficiency tests. Studies are underway to determine how close current drainage volumes are to past estimates. There have been significant changes in the crops grown during the past 40 years, though farming practices and facilities are similar in many respects to past conditions. Farmed acreage has been replaced by some residential development and flooding of some islands (e.g., Franks Tract, Clifton Court). The 1954-55 data is useful as a starting point for studying past seasonal and regional differences in drainage discharge and for modeling current estimates. The patterns help identify major areas

with potentially high sources of drainage and DOC loading.

Figures 4.10 through 4.14 show the 1954-55 monthly drainage estimates for each Delta subunit within each of the three DOC subgroups. Overall, the trends were similar with peak drainage discharge in the summer and late fall-early winter. This pattern corresponds with the peak water demand for irrigation during the hot summers and the ponding of fields to remove salt buildup and rainfall in November to March.

The drainage volume is relatively lower in the southern mineral region which includes areas classified as the low DOC subgroup. The highest drainage areas are in units 18, 20, and 22 which are in the high DOC subgroup. Work is underway to measure drainage discharge volumes to determine if the 1954-55 estimates can be used as reasonable estimates of current conditions in a normal water year.

Fig. 4.10. DOC Subgroup 1 Drainage

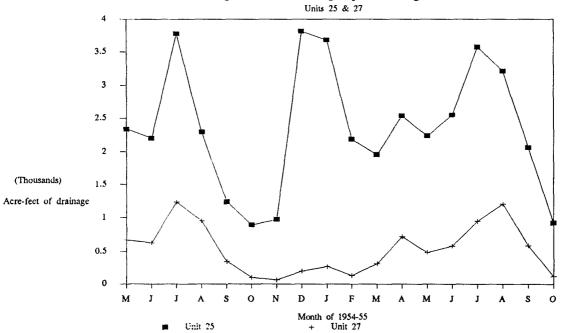


Fig. 4.11. DOC Subgroup 2 (South) Drainage

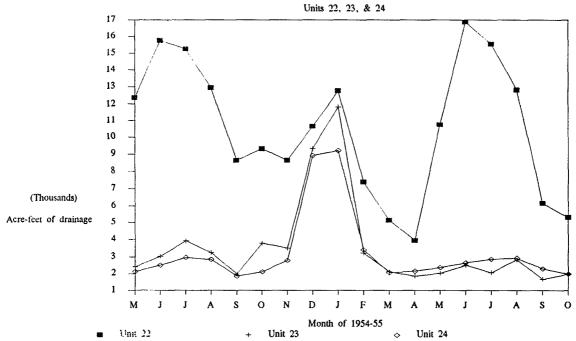


Fig. 4.12. DOC Subgroup 2 (North) Drainage

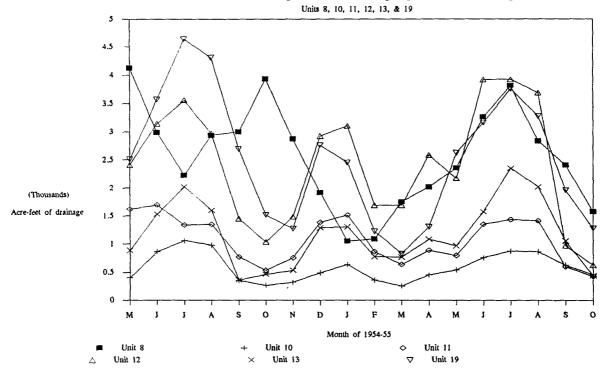
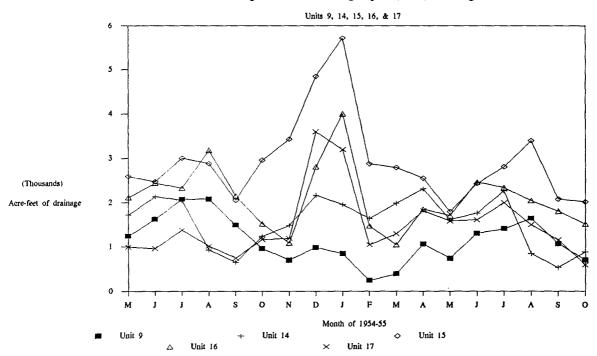
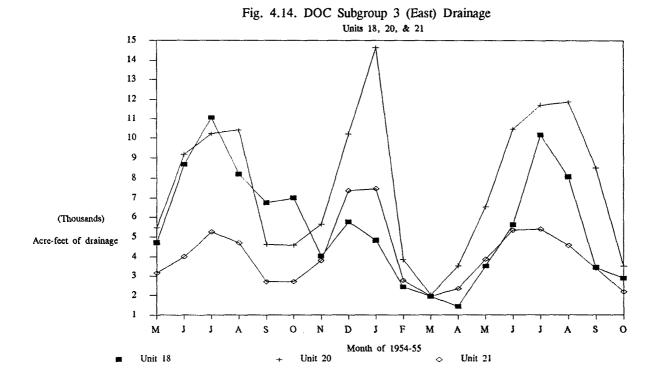


Fig. 4.13. DOC Subgroup 3 (West) Drainage





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Seasonal Factors

Drainage volume, DOC concentrations, and the characteristics of DOC in the drains could be explained by seasonal agricultural practices and climate. Irrigation follows the needs of the growing crops and weather. Summer drainage volume will be high during the hot summers because of increased irrigation. Drainage volumes are high in the late fall and early winter when farmers flood the fields to remove salt buildup in the soil or to create temporary waterfowl habitat for wetlands experiments.

Fresh organic matter will be less UV absorbing than older humics. As organic matter decomposes, more UV absorbing humics will form and DOC will decrease as some is lost as carbon dioxide. This changes the UVA to DOC ratio, which is specific absorbance. Therefore, older material will have higher specific absorbance than younger decaying organics. If drain water specific absorbance increases are the result of the biotransformation of organic matter into the UV absorbing humic compounds, then seasonal ratios also indicate increased microbial activity in the decomposition of organic matter.

Specific absorbance (UVA:DOC ratio) changes as carbon is lost from DOC as CO2 and UVA compounds are left behind.					
Fresh decaying organics	=====>	Older humics			
UVA value low per mg/L DOC	====>	UVA value higher per mg/L DOC			

As a general rule, a 10 degree Celsius rise in temperature within an organism's tolerance limits will double its metabolic rate. Air temperatures in the Delta often exceed 100 degrees Fahrenheit in the mid-summer afternoons and are below freezing in the winter nights. Therefore, microbial decay is slower in the cooler period and much more rapid in the warmer months. Over time, some DOC is lost to the atmosphere as carbon dioxide gas, and the remaining material is transformed into humic-type materials. This would explain the change in the UVA:DOC ratio of a sample over time as DOC is reduced and more UV absorbing humics increase.

A recent USGS study (Deverel and others, 1994) showed that spatial and temporal variabilities in CO₂ fluxes from Delta fields are due to varying soil temperature, percentage of soil

organic matter, plant-root respiration, and soil-moisture content (Deverel et al., 1994). High soil moisture content causes lower soil temperatures, anaerobic conditions, and reduced diffusion of CO_2 and oxygen that helps reduce CO_2 production. The amount of CO_2 produced from the oxidation of organic matter ranged from 40 percent to 91 percent. These patterns indicate the amount of microbial activity in the fields. The study also pointed out that high organic loads from the fields coincide with the seasonal water table elevations. High DOC in drain water occurs as the water table rises close to the land surface in the winter and early spring and is in prolonged contact with well-decomposed organic matter.

The concentration of DOC in water due to evaporation or evapotranspiration does not appear to be a significant factor for causing higher DOC or THMFP concentrations in drain water. This conclusion is based on data that show January DOC and THMFP increases when evaporation is lowest. Water saturation of soil is believed to be the primary factor for causing high DOC and THMFP in drain water. DOC in drainage water is the result of oxidation and dissolution of organic matter.

DOC concentrations in the drainages are highest in the winter (January - March). This is attributed to the practice of flooding and ponding of fields to leach out salts from the soil. Soil to water contact time is long, so the leaching of organic matter from the fields is maximized. A USGS study showed as much as 125 mg/L DOC was initially released by leaching a Twitchell Island peat soil surface core (Wang, pers. comm. 1993).

There is also a fall (October) increase in drainage DOC. This could reflect decaying crop residues that lie in the fields after the fall harvest and are blown into the open drains by strong winds. It also could be drainage from the last irrigation, which was not pumped out, or drainage from seepage.

Typically, the specific absorbances are more variable in the winter and more stable during the warm summer. The winter ratios indicate a slow decaying mixture of fresh organic matter, the summer ratios indicate rapid decay.

The seasonal climate, farming practices, and other factors that help explain observed DOC levels, drainage volume, and specific absorbances are summarized in Figure 4.15 and Table 4.2. This is a conceptual model of the primary factors that control DOC availability from Delta soils.

Figure 4.15. Seasonal Farming Activities in the Delta

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Table 4.2. Seasonal Factors Affecting Delta Drainage DOC

MONTH	CLIMATE /1	FARMING ACTIVITY /2,3	DRAINAGE VOLUME DISCHARGED	DRAINAGE DOC LEVELS	DRAINAGE UVA:DOC RATIOS	AVAILABLE CROP BIOMASS	SOIL AND WATER MICROBIAL ACTIVITY /4
October	warm	harvest	low	increasing	less variable	fresh crop residues in fields	high
November	cooling		low	high	variable		slowing
December	cooling	leach and flood fields to remove salt	increasing	peak	highly variable	decaying in ponded fields	slow
January	cold-wet	continue leaching	peak	peak	highly variable	decaying in ponded fields	slowest
February	cold-wet	continue leaching	peak	peak	highly variable	decaying in ponded fields	slowest
March	cold-wet		decreasing	high but falling	highly variable		increasing
April	wet and warming	prepare fields and plant	increasing	decreasing	variable		increasing
May	warming	seed and irrigate	increasing	decreasing	variable	growing crops	increasing
June	warm	irrigate	high	low	less variable	growing crops	peak
July	hot	irrigate	peak:	lowest	stable	growing crops	peak
August	hot	irrigate	peak	lowest	stable	growing crops	peak
September	hot	harvest	decrease	low	stable	fresh crop residues	peak

Corresponding factors or measurements:

- 1. Seasonal soil temperature ranges will coincide with the climate.
- 2. The degree of water saturation in the soil will depend on climate, rainfall, and irrigation.
- 3. The length of contact time of soil to water on the Delta islands are primarily dependent on irrigation and drainage practices on the islands.
- 4. Measured CO2 flux (i.e., release or production) is related to the microbial oxidation of organic matter in the soil.

Drainage Organic Carbon Releases

The combined effects of the drought and the releases of organic matter into the channels from drainage were assessed. Available monthly river flow, DOC, TFPC, and drainage volume data were used to estimate carbon concentrations in the Delta channels. TFPC was computed from TTHMFP results. Several assumptions were made to adjust for the lack of data from unsampled areas and for current drainage volumes. Drainage volume data from 1954-55 were used (DWR, 1956).

An earlier estimate of the drainage portion of TFPC in the channels for water year 1988 was presented in the 1990 Delta Island Drainage Investigation Report of the Interagency Delta Health Aspects Monitoring Program (DWR, 1990). With some exceptions, the new, revised method for deriving annual TFPC and DOC levels during 1987 through 1991 is similar to the earlier method. The new approach had the benefit of using more data in the analysis.

A simple model was used to generalize the input of organic matter in the Delta. The "Delta" was treated as a well-mixed basin with water quality represented by data averaged from four stations: Rock Slough at Old River, Clifton Court Forebay intake, Middle River at Borden Highway, and the DMC intake. River inflow was represented by data from the Sacramento River at Greenes Landing, San Joaquin River near Vernalis, Cosumnes River near Dillard Road, and Mokelumne River near Woodbridge. Drainage input was computed by dividing the drainage monitoring data into two groups of islands based on soil type and 1954-55 drainage volume (Figure 4.16).

More sophisticated computer simulation models using flow and water quality data at a network of stations in the Delta are being developed by DWR (Hutton and Chung, 1992). These are not discussed here.

The main assumptions that were adopted to make the revised estimates were:

1. Present monthly drainage volumes are nearly the same as those reported in the 1954-55 study. Therefore, these monthly volumes can be repeated for each year (1987-91). Additional calculations included a ± 10 percent change in drainage volume (i.e., 90 percent and 110 percent of 1954-55 volumes) to provide a range of predicted drainage impacts.

- 2. Drainage DOC and TFPC data at sampled sites can be extrapolated to unsampled drain sites based on soil type and region within the Delta.
- 3. Monthly flow weighted DOC and TFPC data from various island drains can be used to represent total Delta island drainage concentrations. Drainage DOC and TFPC data were averaged by month to produce a 12-month data set. This data set was used in the calculations for each of the five years (1987-91).

INFLOW SOURCES

Sacramento River at Greenes Landing Cosumnes River near Dillard Road Mokelumne River near Woodbridge San Joaquin River near Vernalis

> 1987-91 DAYFLOW records 1987-91 DOC & TFPC data

INTERMEDIATE ORGANIC & MINERAL SOIL SOURCES 1954-55 drainage volume estimates 1987-91 DOC & TFPC data

PEAT SOIL SOURCES 1954-55 drainage volume estimates 1987-91 DOC & TFPC data



THE "DELTA"

Rock Slough at Old River Clifton Court Forebay intake (channel) Middle River at Borden Highway Delta Mendota Canal intake

Figure 4.16. Simple Delta Model

- 4. Delta channel water quality can be represented by averaging the monthly data from four stations in the southwestern Delta.
- 5. TFPC concentrations in the Cosumnes and Mokelumne Rivers have not significantly changed since 1984. Monthly data from these two sites were repeated in calculations for each year of the five years under study, because there were no recent data.
- 6. Flow weighted monthly DOC and TFPC data collected from the Sacramento, San Joaquin, Mokelumne and Cosumnes Rivers represent that which would exist in the Delta channels in the absence of island drainage or other factors that impact water quality.
- 7. The difference between the concentrations of TFPC and DOC in the Delta channels and river inflow water is mostly from agricultural drainage. Simply stated, drainage contribution is equal to the river inflow levels subtracted from the higher Delta channel concentrations. Though agricultural drainage is not the only contributor, this assumption will enable DWR staff to compare the importance of drainage to other sources such as channel algae, riparian vegetation, and sediments.

DOC and TFPC concentrations in the channels were predicted from drainage data. These predicted values were then compared against observed data in the channels. Inflow loadings of DOC and TFPC were also compared against observed values. Details on how the assumptions and computations were made are described in detail in Appendix A, "Methodology Used to Estimate Drainage DOC and TFPC Releases."

Findings and Observations

- A progressive increase of carbon concentrations in the Delta channels was not evident during the five consecutive dry years. The highest carbon concentrations occurred either in drainage or in the rivers and channels during heavy precipitation. During the summer, carbon concentrations were lower in all waters.
- 2. Predicted and observed DOC and TFPC concentrations did not compare well on a

month-to-month basis. There was closer agreement between predicted and observed data when the monthly carbon concentrations were averaged either for a calendar year (i.e., average of all 12 months) or for the same months averaged for the total five-year study (i.e., all January months, all February months, etc.).

During the five-year study period, the predicted and observed DOC monthly concentrations for the "Delta" (i.e., four stations in the simple model) averaged 3.55 and 3.52 mg/L, respectively. The averaged monthly concentrations for inflow DOC was 2.45 mg/L. The predicted effect of agricultural drainage was that the concentration of DOC in channel water would increase by 1.1 mg/L. This predicted channel water DOC concentration was close to the observed channel water DOC. Figure 4.17 shows the five-year monthly averaged DOC concentrations for the "Delta" and freshwater inflow. The predicted concentrations were based on using 100 percent of the estimated island drainage flow of 1954-55.

Figure 4.18 is based on relative concentrations and shows the predicted monthly and observed DOC in the "Delta" in terms of percent increase above freshwater inflow concentrations. There are three predicted values based on 90 percent, 100 percent, and 110 percent of the island drainage flow. Averages for the study period show the predicted drainage impact nearest to the observed DOC was calculated using 110 percent of the island drainage flow. This prediction shows a 55 percent increase above inflow concentrations, whereas the observed increase was 54 percent. If these calculations accurately represent the Delta, then drainage volumes may be 10 percent higher than the 1954-55 estimates or the volumes remain the same and the channels are contributing 10 percent of the DOC.

3. During the study period, the predicted and observed "Delta" TFPC monthly concentrations averaged 3.50 and 3.86 µmoles/L, respectively. The averaged inflow TFPC was 2.42 µmoles/L. The predicted TFPC is 1.08 µmoles/L higher than the inflow TFPC. Observed TFPC is 1.44 µmoles/L greater than the inflow TFPC. The predicted TFPC underestimated the observed TFPC by 0.36 µmoles/L. This may indicate the significance of other sources of carbon such as channel sediments, algae, and riparian plants. Figure 4.19 shows the five-year averaged TFPC concentrations for the "Delta" and freshwater inflow. These

Fig. 4.17. Delta and Inflow DOC

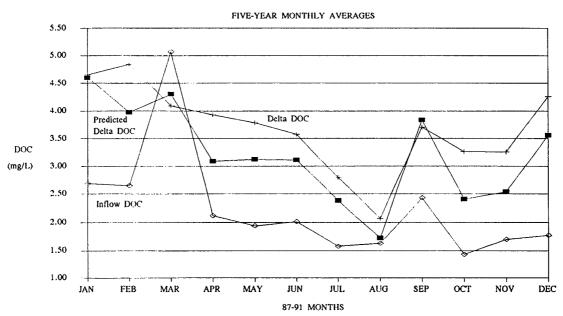
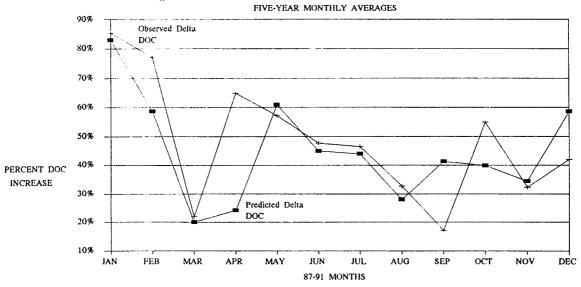


Fig. 4.18. Predicted vs. Observed DOC Increase



predicted concentrations were based on 100 percent of the estimated island drainage flow of 1954-55.

Figure 4.20 is based on relative concentrations and shows the predicted and observed "Delta" monthly TFPC in terms of percent increase above the freshwater inflow concentrations. There are three predicted values based on 90 percent, 100 percent, and 110 percent of the island drainage flow. Averages for the study period show the predicted drainage impact nearest to the observed TFPC was calculated using 110 percent of the island drainage flow. Results of the calculations show that if agricultural drainage from the Delta islands was the sole TFPC source, it increased the concentration of TFPC in Delta channels by 56 percent during the five-year period. The observed average percent increase above the inflow concentration equaled 79 percent. For the five-year period of study, the averaged monthly TFPC predicted was 23 percent less than the average observed TFPC concentration.

THM formation potential of waters containing over 20 mg/L DOC was regularly underestimated as a result of problems with the assay method. Of the Delta waters sampled, results of some drainage water samples were affected. Although a correction factor was developed and applied to the trihalomethane data before the TPFC was calculated, the remaining data scatter indicates TFPC in drainage water is still being underestimated. The resulting low TFPC would certainly cause the predicted impacts of drainage water to be lower than the observed concentrations.

4. On several occasions, concentrations of DOC and TFPC in the Sacramento River were higher than the measured concentrations in the Delta channels. These data probably are not representative of the quality of the Sacramento River for the total month, as the data came from grab samples. A review of precipitation data for Redding and Oroville weather stations revealed that the higher concentrations occurred during months of precipitation north of Sacramento, except September 1987 and 1988. The source of the high carbon concentrations in the Sacramento River during September 1987 and 1988 could have been from upstream rice field drainage, which occurs at that time of the year.

Fig. 4.19. Delta and Inflow TFPC

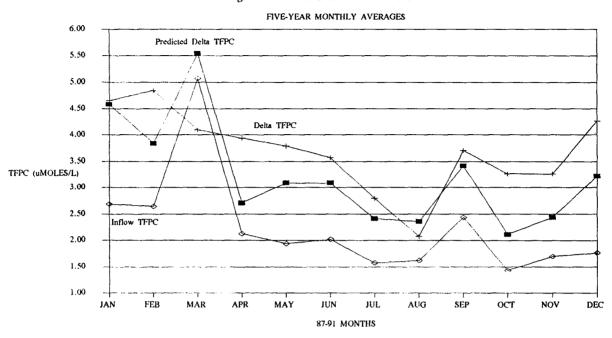
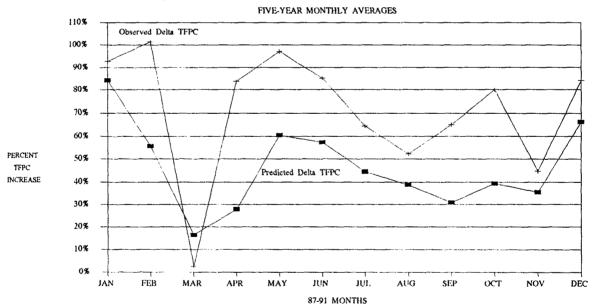


Fig. 4.20. Predicted vs. Observed TFPC Increase



Discussion of Results

The predicted and observed "Delta" DOC and TFPC concentrations were calculated as a percentage of the respective inflow concentrations for each month of the study period. The percentages are derived by subtracting the average river inflow concentration from the predicted channel concentration and dividing the result by the inflow concentration.

The predicted and observed percentages, when compared, exhibit differences in the range of 1 percent to greater than 100 percent. This comparison indicates that the prediction method and/or data, when used for monthly predictions, is inadequate. Obviously, the prediction method is unrefined and does not deal with the dynamic factors of the Delta system. Grab samples are perhaps the greatest source of discrepancy, because they measure the quality of a stream or channel only at the moment the sample is collected. Improvement of the monthly predictions may be achieved by the use of automatic samplers or development of a surrogate parameter that can be continuously monitored. These monitoring methods would provide data more representative of monthly water quality.

TFPC predictions, when averaged for each year and compared with observed Delta channel TFPC concentrations, consistently underestimated drainage effects from 8 percent to 40 percent. Averaging the monthly predicted and observed concentrations for DOC for each calendar year shows no more than a plus or minus 5 percent difference when comparing them on an annual basis. This observation does not include 1991, for which data were missing for October, November, and December. These comparisons demonstrate that the monthly DOC estimates are, almost equally, over and under the monthly observed channel quality.

DOC and TFPC data were subjected to the same flow weighting and estimating equations, yet the DOC predictions are much closer to the observed value than are the TFPC predictions. In addition to the trihalomethane analysis method underestimating the trihalomethane formation potential of waters having DOC greater than 20 mg/L, other factors may affect the TFPC calculation. One factor could be that the TFPC data are not as accurate or reproducible as DOC data. TFPC is calculated from trihalomethane formation potential which does not measure all the carbon present in the water sample and which has detection levels in the part per billion range. Unlike TFPC, DOC is a direct measurement and is present in water in the parts per million range. In general, water constituents in high concentrations are more easily and accurately measured than those in low concentrations. DOC data appear to be a better parameter than TFPC for studying

the release of organic material from agriculture drainage.

Recommendations

- 1. Pursue further studies to identify a surrogate measurement such as specific absorbance for continuously monitoring the organic carbon in Delta waters.
- 2. If the grab samples continue to be the primary method of sample collection, samples should be collected more frequently than once per month during months of precipitation. Using automated sampling devices may be a viable option.
- 3. The quality and quantity of flows in the Mokelumne and Cosumnes rivers are insignificant in calculating the predicted impact of island drainage. The use of these data in future calculations is not necessary or critical to the estimates.
- 4. Revised estimates on the amount of drainage entering the channels will help assess the contribution of organics from drainage as well as from other Delta sources.

 Updated information should be used in future refinements to these estimates.

Modified THMFP Assay

The THMFP assay was developed during 1981-83 by DWR with the guidance of the Interagency Delta Health Aspects Monitoring Program Technical Advisory Group to compare levels of THM precursors in a wide range of Delta waters. The adopted method was a modification of EPA Method 510.1, "The Determination of the Maximum Total Trihalomethane Potential" (1982). ¹

The Original TTHMFP Assay--The original TTHMFP assay is performed as follows: sample water is collected and spiked to a concentration of approximately 120 mg/L chlorine with sodium hypochlorite and incubated at 25°C for seven days (168 hrs). Samples are then quenched with sodium thiosulfate and analyzed for trihalomethanes using EPA Method 601 or equivalent. The assay was designed to meet the following criteria:

- 1. It must be simple enough for large-scale monitoring.
- 2. It must work on a variety of water types with complex matrices ranging from relatively clean American River water to agricultural drain water with high DOC concentrations.
- 3. The chlorine spike concentration used in the assay must be high enough to ensure a residual after seven days of incubation (Samples with no chlorine residual were considered invalid).
- 4. The results must be useful for comparing water sources for planning purposes.

<u>Limitations of the Original Assay</u>--Although the original TTHMFP assay appeared to produce consistent results of good quality, a number of possible limitations have been noted since it was developed:

For the purposes of this discussion the following definitions apply: a) THMs refer to trihalomethanes. b) THMFP refers to trihalomethane formation potential concentrations which are reported by various researchers, including DWR. The word "total" is considered redundant in this case, and most literature does not include an extra "T". c) TTHMFP or TTHMFP assay refers to the original name used in the modified EPA "Maximum Total Trihalomethane Potential. It is a reference to the analytical method developed by DWR, rather than the products.

- 1. There was concern that the THMs formed by the assay might be a function of the chlorine used or that low DOC samples might have a relatively higher fraction of DOC converted to THMFP than high DOC samples.
- 2. The original assay specified EPA Method 601 for analysis of THMs. This waste water method was specified, because agricultural drainage more closely resembles waste water than raw drinking water. Method 601 includes a cleanup step which addresses this problem. However, Method 601 has limited quality control requirements as compared to the EPA 500 series methods.
- 3. The yield of THMs is pH-dependent. The original DWR TTHMFP Assay does not include buffering the sample pH, nor is pH measured.
- 4. Other constituents, particularly ammonia, can interfere with the assay by actively competing for Cl₂, reducing the effective initial dose.
- 5. Bromides complicate the interpretation of the TTHMFP assay by increasing the weight of total THMs formed. This happens by two mechanisms: (a) brominated THMs simply weigh more than chlorinated THMs, and (b) bromide may increase the molar yield of THMs produced in the assay.

Some of the concerns associated with the original TTHMFP assay could be addressed administratively by changing the EPA method to improve sensitivity.

To address the complications due to bromide, the Department adopted a measure of THMFP which is intended to focus more on the organic portion of THMs and remove variations due to the differing weights of chlorine and bromine. TFPC, or "THM Formation Potential as Carbon," is the carbon content of THMFP expressed as ug/L carbon. It is proportional to molar THMFP.

TFPC has the added advantage of eliminating the temptation to inappropriately compare assay results directly with drinking water standards or THMs measured in treated water. TFPC also appears to be a stable parameter which can successfully be used by DWR modelers in predicting THM precursors (as TFPC) at export stations. For purposes of comparison, TFPC

concentrations are approximately 10 percent of the THMFP concentration.

Modified SDS THM Assay--In 1991, DWR and some members of the MWQI advisory committee began determining ways the TTHMFP assay could be improved.

One suggestion was to modify the TTHMFP assay to make it more like a Simulated Distribution System (SDS) THM measure, with a Cl₂ dose calculated as a fixed ratio based on DOC and NH₄ concentrations. The proposed assay produced excellent analytical results, but had some drawbacks:

- 1. Results measured something less than the "Maximum Potential THMs" so were not directly comparable to the original THMFP assay.
- 2. Analysis required measuring both DOC and ammonia, then calculating a specific chlorine dose for each and every sample analyzed. This is impractical for large numbers of samples analyzed in the MWQI Program.
- 3. Some high DOC samples might require impractically high doses of Cl₂.

<u>Characteristics of the Original THFMP Assay</u>--DWR embarked on studies to evaluate the characteristics of the original TTHMFP assay and, if necessary, update the procedure to address as many of the limitations of the original assay as possible. Staff also thought any modified assay should yield results comparable to those in the old assay, where the above limitations were not significant.

A series of studies were devised and performed at the Metropolitan Water District of Southern California and DWR to explore the limits of the original TTHMFP assay and to develop a modified assay. The studies looked at a number of factors, including:

- 1. Sensitivity of TFPC to bromides;
- 2. Effect of buffering TFPC formation;
- 3. Linearity of TFPC measurements with dilution;
- 4. Sensitivity to Cl₂ dose; and

5. Improved relationship between TFPC versus DOC and UVA_{254nm} measurements.

The tests were designed to look at ranges of DOC and bromide which are encountered in the Delta. Major findings from the studies included:

- 1. Sensitivity to Bromides: TFPC formation increased by about 10 percent when 0.50 mg/L Br was added to a sample from the Sacramento River at Greenes Landing. Bromide levels in Sacramento River at Greenes Landing are about 0.01 mg/L. Therefore, the bromide concentration had to be increased by 50 times (5000 percent) to obtain a 10 percent increase. TFPC results are affected by bromide concentrations but probably not to a large degree.
- 2. Effect of Buffering and pH: The study showed that:
 - a. pH had a measurable effect on TFPC yield;
 - b. pH increases with increased Cl₂ dose and decreases with increased DOC level;
 - c. pH of spiked and incubated channel water samples was about 8.2, similar to buffered samples in the modified assay described below; and
 - d. Buffering of the Cl₂ spike solution brought a majority of samples to pH 8.2. The remainder were brought near pH 8.2.
- 3. Linearity of TFPC measures with dilution: A number of experiments showed that:
 - a. Analyses of samples with DOC levels below approximately 20 mg/L showed consistent results for all dilutions (using the normal 120 mg/L Cl₂ dose);
 - b. Samples with DOC much above approximately 20 mg/L appear to have incomplete conversion of DOC to TFPC using the 120 mg/L Cl₂ dose. However, dilution of these samples anywhere below approximately 20 mg/L DOC produces consistent, and higher, TFPC yields.
- 4. Sensitivity of high TFPC to Cl₂ Dose: The study showed that:

- a. For a given level of DOC, TFPC production increases with increased Cl₂ dose until it reaches a "Maximum TFPC" related to the original DOC level. After that point, increased Cl₂ dose does not produce higher TFPC;
- Samples above approximately 20 mg/L DOC required more than 120 mg/L Cl₂ dose for complete production of TFPC or else the sample had to be diluted.
 Therefore, high DOC samples using the original TTHMFP Assay probably underestimated TFPC; and
- c. Measurable Cl₂ residual is <u>not</u> sufficient to determine that all precursors have been converted to THMs.
- 5. Improved Relationship between TFPC vs DOC and UVA_{254nm}.

The original TTHMFP assay indicated that DOC and TFPC were poorly correlated in high DOC waters. Dilution studies showed that DOC and UVA_{254nm} are both correlated with TFPC for all DOC ranges, although the exact correlation varies somewhat by water source.

The TFPC Assay--Based on the findings described above, DWR has adopted a modified TFPC assay which addresses most of the concerns about the original TTHMFP assay. Figure 4.21 illustrates the differences between the original and the modified assays.

The new assay, named the TFPC assay, is conducted as follows: Samples are collected and first analyzed for UVA_{254nm} . Samples exceeding $0.6~cm^{-1}~UVA_{254nm}~(\approx 12~mg/L~DOC)$ are diluted to about a $UVA_{254nm}~equal~to~0.5cm^{-1}~(\approx 10~mg/L~DOC)$. Samples are then spiked with a buffered Cl_2 solution to 120~mg/L and incubated for 168~hours. The samples are then quenched and analyzed using EPA Method 502.2, or equivalent. Certain other procedures have been modified to improve the quality control of the analysis. Analyses are reported corrected for dilutions.

Advantages of the TFPC Assay--The new assay addresses most of the concerns raised about the original assay, and has several advantages, listed here.

1. Results from the TFPC assay are directly comparable to results from the original

TTHMFP assay for samples with DOC below approximately 20 mg/L. Samples analyzed by the original method were not buffered to pH 8.2; however, DWR studies indicate that "low" DOC samples tend to naturally fall into this range when spiked, anyway.

- 2. The method remains relatively simple to do, and depends only on measurement of UVA_{254nm} to determine dilutions. The UVA measurement is simple, fast, and inexpensive.
- 3. TFPC results from the TFPC assay are valid over the entire range of DOC encountered by the MWQI Program.
- 4. The assay is not sensitive to reasonable variations in Cl₂ dose because it ensures that the Cl₂:DOC ratio is high.
- 5. Method QC for the new assay is improved because samples are analyzed by method 502.2 or equivalent.
- 6. Samples are buffered at pH 8.2, eliminating variations in analytical yield due to differences in pH.
- 7. Potential effects of ammonia, which are not measured beforehand, are addressed by the comfortable excess in Cl₂ dose for a given DOC range. Tests showed that the 120 mg/L Cl₂ dose was sufficient for DOC concentrations up to approximately 20 mg/L. DOC (as predicted by UVA_{254nm}) in the new test is not allowed to exceed approximately 12 mg/L. The excess available Cl₂ is sufficient to neutralize the NH₄ levels encountered in the Delta. High DOC samples are diluted before inoculation, which also dilutes NH₄ and its demand for Cl₂.

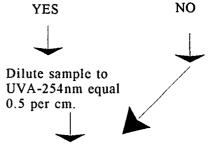
Figure 4.21.

Old THMFP and New TFPC Methods

ORIGINAL TTHMFP ASSAY METHOD from 1982 to June 1992

NEW TFPC ASSAY METHOD adopted July 1992 with additional lab QC protocol

Is sample UVA-254nm > 0.6 per cm?



Spike with buffered sodium hypochlorite solution to achieve chlorine dose of 120 mg/L and pH = 8.2

Incubate at 25 deg. C. for 168 hrs. (7 days)

Measure pH

Quench (dechlorinate) with sodium thiosulfate

If chlorine residual is present continue. If not the test is invalid.

Measure THM using EPA Method 502.2 or equivalent

Compute sum of carbon concentrations of the four THMs and correct for any dilution. Report results as the THMFP Carbon or TFPC.

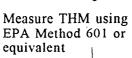
Spike with unbuffered sodium hypochlorite solution to achieve chlorine dose of 120 mg/L

Incubate at 25 deg. C. for 168 hrs. (7 days)



Quench (dechlorinate) with sodium thiosulfate

If chlorine residual is present continue. If not the test is invalid.



Compute sum concentration of THM as Total THM Formation Potential

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<u>Limitations of the TFPC Assay</u>--The limitations of the assay are:

- 1. TFPC yield is affected by bromide concentration, although the effect is relatively small. Other THM assays are also affected by bromide concentrations;
- 2. Although the assay is valid over a wide range of DOC concentrations, very high DOC concentrations may require special precautions because high dilutions are needed; and
- 3. Waters with high levels of NH₄ or other substances which compete for Cl₂ may not yield the maximum potential TFPC.

Comparability of TTHMFP vs. TFPC Assays—A number of analyses were collected in June 1992 and analyzed by the old and modified methods, and their results compared. Old and modified method analyses were comparable within method limits for DOC less than about 20 mg/L. All samples in this region fell along a line.

Above 20 mg/L the TFPC reported by the original method fell below the line and leveled off. Apparent yield of TFPC from the 75 mg/L DOC sample is not much higher than from the 25 mg/L sample. This is the same behavior predicted by the dilution and spiking experiments. Conversely, the modified method TFPC yield continued to follow the general DOC:TFPC relationship over the entire range of DOC.

Chlorine residuals for all samples were positive, but the original method analyses of samples greater than 20 mg/L yielded low residuals of 20 mg/L or less Cl₂. All samples which demonstrate a full conversion of TFPC had Cl₂ residuals of 40 mg/L or higher.

Previous Underestimations of THMFP

Laboratory studies on the effects of chlorine dose on THM formation led to a re-evaluation of the DWR raw water THMFP assay (Reckhow and Edzwald, 1991; Symons, 1991; Krasner, 1992). The assay was developed to compare the relative maximum THMFP of various water types (e.g., drainage, fresh water, and sea water) under a specific test condition. The assay has been modified in pH and chlorine dosage procedures to improve comparable results, since earlier tests were not buffered and chlorine dosage was fixed at 120 mg/L regardless of DOC

concentration (Agee, 1992).

Groups of samples with DOC above 20, 30, and 40 mg/L were compared against their respective THMFP results. The data indicated a strong likelihood that the TFPC of samples with more than 20 mg/L DOC could have been underestimated because of insufficient chlorine to drive the reactions to completion. DOC and TFPC plots showed that the TFPC of samples with DOC concentrations above 20 mg/L began to fall below the regression line extrapolated from samples with under 20 mg/L DOC.

DWR was also concerned that THMFP or TFPC would be overestimated because of overchlorination. Channel waters generally have DOC between 2 and 10 mg/L. High chlorine dosages (120 mg/L) might convert recalcitrant organics or precursors of other DBPs to trihalomethanes. Laboratory studies were conducted to study the effects of chlorine dose and residual chlorine on TFPC. Samples were dosed with different chlorine amounts. The results showed that at the end of the seven-day test the residual chlorine of samples that had met their chlorine demand were nearly the same. The TFPC did increase slightly at the higher chlorine doses. However, since DWR tests are used to compare the relative differences in TFPC between drain and nondrain samples, the overestimation is not significant enough to alter conclusions about these differences. The TFPC of the samples that received high chlorine doses were within the same range of those that met the new recommended chlorine dose based on DOC and ammonia concentrations in the samples.

Recent advances in the study of disinfection by-product (DBP) formation and control by the water industry have been invaluable for the interpretation of this report's THMFP data. The earlier attempt to understand the tendency of a water sample to form brominated THMs was made by computing a Total Bromomethane Formation Potential (TBFP). New information shows that the distribution and formation of the four THMs are affected by chlorine dose and other test conditions. However, the amount of THM precursor carbon that is incorporated in THM formation is unchanged. Based on these findings, the TBFP term is no longer used.

Surrogate Measurements

The use of a surrogate measurement could be a valuable and inexpensive screening tool in assessing raw water quality (Dobbs et al., 1972; Edzwald et al., 1985; AWWARF, 1988). Strong

relationships were seen between UVA_{254nm} measurements and DOC concentrations in most Delta island drainage and channel water samples. However, the degree of accuracy varies widely, so UVA measurements cannot always be used as a reliable substitute for DOC analyses.

The variability is probably caused by the mixed nature and sources of DOC that occur over time. Drainage DOC comes from drained soils and fields while channel DOC sources include algal exudates, sewage, riparian vegetation and debris, biota, and drainage from various regions. The nature of DOC in the channels is more likely to change more frequently (e.g., from tides, hydrology) than the DOC of a drainage canal. Differences between drain and non-drain Delta water samples have been seen in the distribution of the apparent molecular weight and THM formation potentials (Amy, et. al., 1990). This is not to say that drainage DOC composition is fixed. Drainage DOC varies with season depending on farming activities and the seasonal variables discussed earlier. Changes in specific absorbance serve to illustrate these points.

At some Delta channel stations, UVA_{254nm} measurements show strong promise as a substitute for laboratory DOC analyses. A potential application might be devising in-situ or continuous UVA_{254nm} monitoring instruments at some channel stations or intake facilities. Some sort of self-cleaning filtration device is needed, as current UVA measurements are taken of filtered samples. Different UVA to DOC regression equations probably exist for different channels in the complex Delta. These will need to be determined.

UVA measurements of drainage samples can be used to estimate the range of expected DOC concentrations. The predictive value of these measurements is, however, significantly less than that of channel water samples.

The relationships of TFPC to DOC or UVA are directionally linear, but accuracy is limited in some cases because of data scatter. Predicting TFPC for channel or low DOC waters from DOC or UVA data was more accurate than for high DOC drainwaters.

Shifts in the amounts and types of organic matter (e.g., humic materials) may be the major reason for the difficulties in obtaining consistent correlations among UVA, DOC, and TFPC. The underestimation of THMFP or TFPC from using the earlier DWR THMFP assay method may be another reason. However, studies elsewhere support the former hypothesis. Seasonal differences in the TOC character of an Iowa River water supply was identified as the predominant factor in THM variability, not temperature and pH (Veenstra and Schnoor, 1980). Hoehn and others

(1977) found that the concentration of organics may fluctuate by only a few milligrams per liter from winter or summer but the structure of the organics themselves may be sufficiently varied such that they will yield different THM concentrations when chlorinated.

UVA and DOC Correlations

<u>Drains</u>. Simple linear regression testing showed a strong relationship for each Delta drainage unit (Table 4.3). Drainage DOC concentrations from organic soil areas typically range from 8 to over 100 mg/L with most in the 10 to 40 mg/L range. The ability to predict drainage DOC from UVA is limited but may be acceptable to some applications. The 95 percent prediction limits (outer pair of dashed lines around the regression line in the following figures) indicate the range within which 95 percent of observations will occur for each prediction. The ranges averaged \pm 5 mg/L of the predicted value. The 95 percent confidence limits for the mean regression line are shown as the pair of dashed lines closest to the regression line.

Table 4.3. Drain UVA-DOC Correlations

Delta unit	Degrees of freedom	R2 %	Equation	DOC range (mg/L)	95% prediction limit (est. mg/L)	Figure
15	53	79	DOC = 2.7 + 18.6(UVA)	8 - 56	± 7	4.22
16	41	77	DOC = 1 + 20(UVA)	5 - 37	± 5	4.22
17	11	26	poor correlation or insufficient data			
18	32	87	DOC = 3.3 + 17.2(UVA)	8 - 55	± 8	4.22
20	39	91	DOC = -1 + 26.8(UVA)	3 - 90	± 10	4.22
21	14	72	DOC = 11.4 + 10.5(UVA)	9 - 37	± 7	4.22
22	23	97	DOC = 0.4 + 22(UVA)	3 - 35	± 4	4.22
23	15	99	DOC = 0.5 + 22.9(UVA)	6 - 37	±1	4.23
27	31	64	DOC = -0 1 + 43(UVA)	3 - 14	± 3	4.23

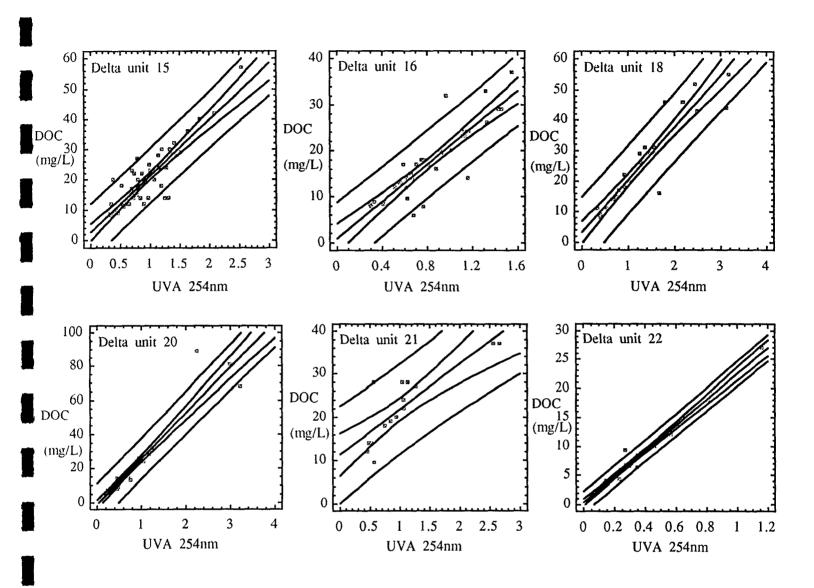
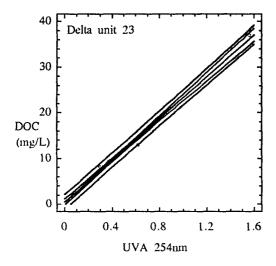


Figure 4.22. Delta Island Units 15 - 22 UVA-DOC Correlations



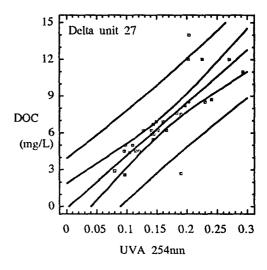


Figure 4.23. Delta Island Units 23 and 27 UVA-DOC Correlations

The good correlations of drainage DOC to UVA_{254 nm} measurements show generally high concentrations of ultraviolet absorbing compounds (e.g., humics) in drainage and fairly consistent proportion of these compounds relative to nonabsorbing organics. Outlying data points may indicate shifts in the amount of UV absorbing organics in the DOC pool. These could be related to the aging of organic material as well as organic content. Unit 27 (Pescadero Tract), which has mineral soil, has less UV absorbing organic matter than the other organic soil tracts. The differences between the regression equation coefficients of Unit 27 (coefficient = 46) and the others (coefficients at about 20) are apparent.

The correlation between UVA and DOC was best for drainages that fell within the intermediate DOC subgroup (Table 4.4). UVA also correlated better with DOC at the predominant UVA:DOC range of a Delta unit than with data that included the other ranges.

Table 4.4. UVA-DOC Correlations with Specific Absorbance

Delta Unit	UVA:DOC Range	Degrees of freedom	R ² (%)	Equation	DOC range (mg/L)	95% prediction limit (est_mg/L)	Figure
15	mid	47	89	DOC = 2.8 + 19.7(UVA)	8 - 58	±4	4.24
15	low	3		Insufficient data			1
15	high	7		Insufficient data			
16	mid	37	88	DOC = 1.7 + 20(UVA)	8 - 37	±4	4.24
16	low	3		Insuffficient data			
27	low	29	73	DOC = 43.5(UVA)	3 - 14	± 2.5	4.24

Specific absorbance (UVA_{254nm}:DOC) ranges: low < 0.03; mid between 0.03 and < 0.06; high > 0.06

In conclusion, UVA can be used to obtain good estimates of the range of DOC concentrations in drain water for most Delta areas. These estimates are best for samples with ratios that are within the predominant UVA:DOC range of a Delta unit. The data did not show that UVA_{254nm} measurements can be used as a substitute for laboratory DOC analyses of Delta island drain water. Accurate determination of DOC requires laboratory analysis.

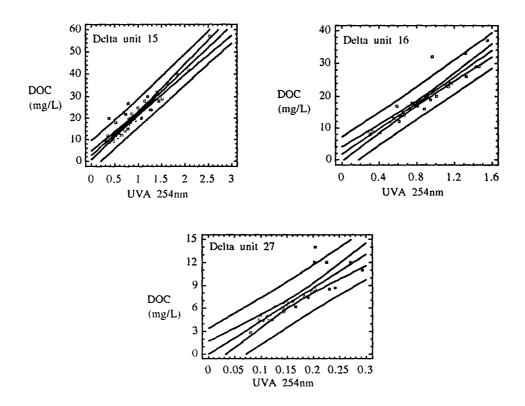


Figure 4.24. Delta Drainage UVA-DOC Correlations

Channels. In general, the use of UVA to predict channel water DOC concentrations appears to be more accurate than for drainage samples (Table 4.5). DOC concentrations typically range from 2 to 4 mg/L in the Sacramento River but increase in the interior Delta channels to 4 to 8 mg/L. The higher DOC concentrations usually occur after winter storms. The 95 percent prediction limits indicate that 95 percent of the observations could be as close as \pm 0.3 mg/L from the prediction value. Simple linear regression results of UVA to DOC for key Delta channel stations are presented below.

Table 4.5. Channel UVA-DOC Correlations

Station name	UVA-DOC range	Degrees of freedom	R ² %	Equation	95% prediction limit (mg/L)	Figure
Greenes	low - med	29	84	DOC = 0.98 + 24.2(UVA)	± 0.6	4.25
Rio Vista	all	55	79.44	DOC = 0.9 + 23.6(UVA)	± 0.4	
Rio Vista	low	46	47.26	DOC = 0.9 + 25.2(UVA)	± 0.45	
Rio Vista	mid	8	95.83	DOC = 29.7(UVA)	± 0.5	
DMC intake	all	49	73	DOC = 0.8 + 26.8(UVA)	± 0.5	4.25
Banks Headworks	ali	53	92	DOC = 0.8+25.4(UVA)	± 0.3	4.25
Banks Headworks	low	21	92.33	DOC = 33(UVA)	± 0.35	
Banks Headworks	mid	37	98.26	DOC = 0.4 + 26.8(UVA)	± 0.1	
Vernalis	all	27	79	DOC = 1.3 + 27 2(UVA)	±04	4 25
Mallard Is.	all	55	21.56	DOC = 17 7(UVA)	±25	
N. Bay Pumping Plant	all	20	23.35	poor correlation or insufficient data		
N Bay Pumping Plant	low	7	87.56	DOC = 41 2(UVA)		
N. Bay Pumping Plant	mid	8	97.09	DOC = 1 + 23.5(UVA)		
Sandmound	all	49	76.91	DOC = 0.7 + 25.2(UVA)		
Sandmound	low	31	88.08	DOC = -1.3 + 53.3(UVA)		
Sandmound	mid	17	95.90	DOC = 24.5(UVA)		
Middle River	all	21	93.86	DOC = 0.7 + 25(UVA)		
Middle River	mid	19	97.86	DOC = 0.52 + 26(UVA)		
CCWD PP1	all	13	42.43	poor correlation or insufficient data		
CCWD PPI	low	9	47.73	poor correlation or insufficient data		

Specific absorbance (UVA254nm:DOC) ranges: low < 0.03; mid between 0.03 and < 0.06; high > 0.06

Similar to drainage, the channel data generally indicate that specific absorbance and the strength of the correlations of UVA to DOC may be related. The correlations improved for samples with mid-range specific absorbance. The intercepts of the linear regression equations where UVA equals zero and intersects the DOC axis can be used to estimate the amount of non-UV absorbing dissolved organics in the samples. High slopes (i.e., large numeric constant multiplied against UVA) correspond to low humic samples (low specific absorbance range). Samples with low-range ratios had about half the slope or UV absorbance per DOC concentration of the mid-range samples. This could mean that mid-range samples had either about twice the concentration of UV absorbing organics (e.g., humics) or had higher UV absorbing compounds than the low ratio samples.

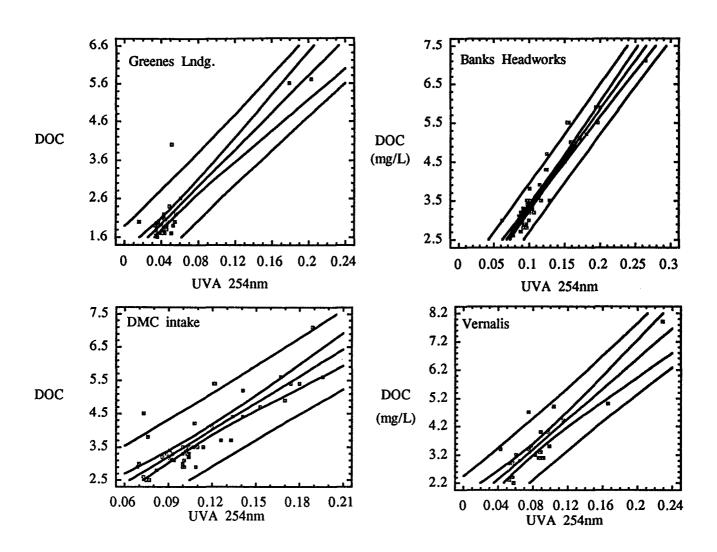


Figure 4.25. Channel Water UVA-DOC Correlations

Mallard Island results showed that the composition of DOC at this intertidal station can be widely variable and significantly different from upstream waters. Humics typically comprise 30 to 50 percent of the DOC in rivers and 50 to 90 percent in colored waters, such as from soil drainage and wetlands (Thurman, 1985).

Channel waters with similar specific absorbance can be chemically different as shown by different strengths of correlation (R²) for the same specific absorbance range. For example, for the low-range, the correlations of UVA to DOC were poor at the Mallard Island and CCWD Pumping Plant #1 stations but better at the some other stations (e.g., Greenes, Vernalis, Banks).

TFPC Correlations

<u>Drains</u>. Regression results show drain water TFPC may be estimated from DOC data (Table 4.6). The strength of some correlations may depend on the UVA:DOC ratio of the sample. However, the results may be in error from underestimations of THMFP or TFPC under the old THMFP methodology. Additional work in progress that uses the new modified THMFP test method will enable refinement of the prediction equations and possible improvements in narrowing the range of the prediction limits. Some of the TFPC to DOC regression results are presented below:

Table 4.6. Drainage DOC-TFPC Correlations

Delta unit	UVA:DOC range	Degrees of freedom	R2 %	Equation where DOC ≤ 40 mg/L	95% prediction limit (est. µg/L)
16	mid ·	38	48.49		± 90
17	mid	9	92.91	TFPC = 7.5(DOC)	± 20
18	mid	23	83.87	TFPC = 53.2 + 6.9(DOC)	± 45
20	mid	37	89.55	TFPC = 31.1 + 7.4(DOC)	± 30
21	mid	9	11.16	poor correlation	
22	mid	31	96.21	TFPC = 26.7 + 7.6(DOC)	± 20
23	mid	12	78.23	TFPC = 51.6 + 4.8(DOC)	± 35
27	low	27	13.20		± 40

Specific absorbance (UVA254nm DOC) ranges: low < 0.03; mid between 0.03 and < 0.06; high > 0.06

<u>Channels</u>. While statistical results of the regression tests were mixed, the plots and ranges of the 95 percent prediction limits showed that channel water TFPC could be better estimated by DOC concentrations than for drain water (Table 4.7). This difference could be explained by the underestimation of THMFP or TFPC of higher DOC drain water samples (above 20 mg/L) under the old DWR THMFP test method.

Table 4.7. Channel DOC-TFPC Correlations

Station name	UVA:DOC range	Degrees of freedom	R2 %	Equation	95% prediction limit (est. µg/L)
Greenes	low	29	8.7		
Rio Vista	all	55	67.7	TFPC = 12.2(DOC)	± 12
Rio Vista	mid	8	80.6	TFPC = 10.5(DOC)	± 18
Rio Vista	low	46	58	TFPC = 16.6(DOC)	± 12
DMC intake	low	23	60.9		
Banks Headworks	low	21	64.5		
Banks Headworks	mid	37	71.4	TFPC = 9.5(DOC)	± 17
Vernalis	low	30	74	TFPC=29(DOC)	± 15

Bromide, Chloride, and EC

Water treatment operators have health concerns about bromide, which can be oxidized to form brominated disinfection by-products such as bromate and bromoform. EPA is considering regulating bromate because of its relatively high carcinogenic potential. Bromide presence may also influence the rate and extent of formation of nonhalogen-containing organic products. Bromide analyses were added to the MWQI Program in January 1990. Because bromide and chloride are major anions of sea water and are in constant ratio to each other, the effect of Bay water intrusion could be tracked in the Delta.

The data showed that bromide concentrations could be predicted from chloride measurements in the brackish waters of the Delta. Electrical conductivity (EC) readings could also be used to predict chloride concentrations.

Other Water Quality Concerns

Selenium

Selenium is a naturally occurring element that, in high concentrations, can cause various deformities in animals and birds. In humans, low concentrations are essential, but high concentrations can produce assorted physical problems such as hair and nail loss, and gastrointestinal problems.

Selenium in the San Joaquin River can be traced back to discharges of Central Valley agricultural drainage. In 1984 the U.S. Fish and Wildlife Service observed young deformed birds at the Kesterson Wildlife Refuge near Los Banos, California. These abnormalities were attributed to high levels of selenium discovered at Kesterson and in the San Luis Drain.

In response to these concerns, monitoring for selenium was started in the San Joaquin River and the Delta. During 1987-91, selenium levels did not exceed the drinking water standard of $10 \,\mu\text{g/L}$. The highest level detected was $9 \,\mu\text{g/L}$ in March 1989 at Maze Road Bridge on the San Joaquin River. Just downstream from the site, a sample taken at San Joaquin River near Vernalis showed a value of $5 \,\mu\text{g/L}$. This drop can be attributed to mixing of the San Joaquin and the Stanislaus rivers, which occurs just upstream of Vernalis. At various other times, readings at the Maze Road station varied between below detection limits to $8 \,\mu\text{g/L}$.

Selenium was detected at the Banks headworks on six occasions, with values ranging between 1 and 3 μ g/L. At the other times, values were below detection limits. At the DMC intake station, selenium was detected on 20 occasions. Values here varied between 1 and 5 μ g/L. These variances between sites indicate the major influence of the Sacramento River at the pumping stations. Banks water is taken from Old River through the Clifton Court Forebay intake. This facility has control gates that allow for the regulation of waters during high and low tide. Another factor is the location of the gates, which are north of the DMC intake facility. The DMC pumps pull more San Joaquin River water into its system than Banks. This is because San Joaquin River water flows into Grant Line Canal and Old River upstream of the DMC intake.

Selenium has been tested at various agricultural drains throughout the Delta. Results at these sites were below detection limits a majority of the time with a few exceptions. Drains on Mossdale Tract showed values ranging from 1 to 4 μ g/L. Within the last three years these drains have been removed from service due to the development of lands on this Tract. Occasionally selenium was detected on Pescadero , Shima , and Egbert tracts, but these sites were dropped from the study to concentrate more on the central part of the Delta. In summary, selenium levels in Delta water supplies easily meet drinking water standards.

Sodium

High sodium levels can harm crops, corrode pipes, and make water undrinkable. People with heart conditions and high blood pressure may need to limit sodium intake. The National Academy of Sciences has two health advisories for daily sodium intake. There is a 20 mg/L limit for persons on severely restricted sodium diets and a 100 mg/L limit for those on moderately restricted diets. There are no State or federal drinking water standards for sodium. Evidence is inconclusive as to whether elevated blood pressure is linked to sodium intake from drinking water, as most sodium intake is from food.

EPA regulations require all public water suppliers to monitor sodium in their drinking water and to report the levels to local authorities (40 CFR 141.14). When sodium levels are high, water suppliers must notify the State Department of Health Services which, in turn, coordinates with local health authorities to inform the public.

The major sodium sources in the Delta include sea water intrusion, local island drainage 108

discharges, and San Joaquin River water. Sea water is naturally high in sodium and enters the western Delta from tidal action and reverse flows. Local drainage is high in salts because of evaporation of applied irrigation water from the channels. Sodium in the San Joaquin River is attributed to Central Valley drainage discharges.

Because San Joaquin River flows were low during the drought (average daily flow less than 1300 cfs), most of the water returned to the Central Valley by way of the Delta-Mendota Canal. Sodium impacts from the San Joaquin River, if any, are probably localized to the southern Delta region along Old River, and Grant Line, Fabian, and Bell canals.

The seasonal pattern shows higher sodium concentrations in the mid-summer through winter months (July - February) when river flows were low and drainage discharges were typically high due to irrigation and field leaching. Sodium levels decreased in March due to heavy rains and river flow.

Sodium levels at the southern Delta channel stations resemble those levels at Banks. In contrast, sodium concentrations average about 10 mg/L at the Sacramento River at Greenes Landing station.

Data Quality Review

As stated in the section titled "Program Description," one major objective of the MWQI Program is to collect long-term monitoring data to assess the temporal and spatial changes in water quality in the Delta, and to identify the causes of the observed changes. To meet that purpose, the quality assurance and quality control (QA/QC) review and evaluation process was conducted to validate the MWQI data prior to data analysis and interpretation to prevent misinterpretations of the data.

MWQI staff, with the assistance of DWR's Quality Assurance/Control Program staff, formed a QC assessment team to review MWQI data collected from 1987-1991. The initial effort required assembling QC data (laboratory and field) pertinent to the study. Printed copies of these data were electronically scanned or key-entered into a computer database. After the entered data had been verified with the printed laboratory QC reports, they were then evaluated by the assessment team by comparing the results against QC criteria.

Overall, the MWQI data set (August 1987 to December 1991) were validated to be acceptable. Over 95 percent of all laboratory quality control checks or analyses performed by the contracted laboratories, Enseco and Pace, met the selected quality control criteria established for the MWQI Program. Some data, which may not have not met the QC criteria, were considered acceptable because of their slight exceedances and the conservativeness of the acceptance criteria. Only a very small portion of the MWQI 1987-1991 data set were considered unusable. The environmental sample data associated with these latter QC batches have been excluded from the MWQI database.

Some samples taken between August 1987 and June 1989 were analyzed by Enseco Laboratory (West Sacramento, California). Enseco analyzed samples for total organic carbon (TOC) and THM formation potential. Enseco analyzed 249 sample batches.

Some samples taken between July 1989 and December 1991 were analyzed by Pace Laboratory (Novato, California). Pace analyzed samples for total residual chlorine and THM formation potential. Pace analyzed 179 sample batches.

DWR's Bryte Chemical Laboratory analyzed water samples for minerals, metals and some organics between August 1987 to December 1991. Occasionally, Bryte also spiked and quenched THM formation potential samples for Enseco.

During the study period, Bryte had not yet developed a computer database for filing QC data; instead, handwritten logbooks were archived. For this review, a random set of data over the five-year study period was chosen on a quarterly basis (1 QC batch per quarter). Bryte Lab staff searched their original work sheets and reported the requested QC information for the randomly chosen data. QC data were documented in a report for a total of 15 batches. The evaluation of Bryte QC data for this report was based on these 15 batches. DWR's Bryte Chemical Laboratory is in the process of becoming more automated, and is now reporting QC data to MWQI routinely.

Most of the holding times of sample batches were in compliance with EPA recommendations. Since THM data are primarily used in this study for determining seasonal and long-term trends in water quality, not accepting THM results from batches which exceeded the holding time may be imprudent. DWR also uses a modified THMFP test which is not identical to EPA's THMFP test. Thus, a strict application of EPA's holding time may not be appropriate in this case.

In addition, although a total of 18 batches exceeded EPA's holding time for purgeable halocarbons of 14 days, a study of THM holding time which was documented in MWQI's June 1990, Delta Island Drainage Investigation Report of the Interagency Delta Health Aspects Monitoring Program, established that a holding period of up to 80 days does not cause a significant loss in THM concentrations. Another important note is that EPA does allow for variances of holding time in cases where a chemical can be shown to be stable for a longer period of time. For the purpose of this report, the THM environmental data from all 18 batches is considered to be acceptable with the understanding that measures will be taken to reduce or eliminate the source of possible error in future work.

Bryte Chemical Laboratory exceeded EPA's recommended holding time for total dissolved solids (TDS) of seven days in two sample batches. However, an extended holding time study performed by Bryte shows that filtered TDS samples may be stable up to three months. Since holding times for these batches were only slightly exceeded, DWR considered the TDS results to be usable.

No contaminants were detected in any of the 407 method blanks analyzed by Enseco for total organic carbon and THMs. Method blank results from Bryte are all acceptable. Method blank analyses of THMFP by Pace, however, were done incorrectly. Blank water used by Pace was suspected to not be free of organics (see discussion of method blanks in Appendix B). All 551 method blank analyses from Pace were, thus, considered invalid.

The accuracy of sample batch analyses was determined by evaluating recoveries of laboratory control samples (LCS) and matrix spikes. Overall, approximately 91 percent of the LCS recovery results were acceptable in terms of the LCS acceptance ranges provided by each laboratory.

Overall, 87 percent of matrix spike recoveries were acceptable in reference to LCS accuracy acceptance ranges. LCS acceptance ranges were used to evaluate matrix spike recoveries because matrix spike recovery acceptance ranges were not available from each laboratory. This conservative practice by MWQI may explain the relatively lower number of acceptable recoveries from matrix spikes as compared to LCSs.

The precision of sample batch analyses was determined by evaluating the relative percent

difference (RPD) of duplicate samples. Overall, 96 percent of Enseco's and Pace's matrix spike duplicate results is within the appropriate RPD limits. Similarly, results show that approximately 97 percent of the LCS duplicate samples is within acceptable precision limits.

Ninety-six trip blanks were analyzed by Enseco. These samples were analyzed for TOC, bromoform, bromodichloromethane, chloroform, and dibromochloromethane. Only eight samples were found to have TOC concentrations which could represent possible contamination. The remaining 88 trip blanks contained nondetectable concentrations of analytes. These results show that contamination, particularly by THMs, is infrequent during sample processing and transport.

Field duplicates were collected occasionally by MWQI prior to 1989. Since 1989, these samples were taken regularly. Enseco, Pace and Bryte laboratories performed 4,256 analyses on field duplicate samples submitted by MWQI during the study period. A total of 45 different analyses were performed for these duplicates. Overall, 96 percent of MWQI field duplicates is within field duplicate precision limits.

The results of the data quality review are presented in Appendix B.

Chapter 5. CURRENT AND PLANNED ACTIVITIES

Numerous studies and activities are underway, and they include:

- 1. Conducting a joint DWR-USGS drainage volume study to revise estimates on the volume of agricultural drainage discharged into the Delta (The study includes estimates based on power consumption records and measured pump flows.);
- 2. Automated sampling (The use of automated sampling devices to collect daily or hourly samples to study the magnitude of water quality changes at a site. This type of information will improve modeling efforts to characterize monthly statistical values such as a monthly mean or median. It will also enable an assessment of whether "synoptic" monitoring done in this program is sufficient to observe water quality changes across the Delta.);
- 3. Sampling for new EPA regulated contaminants;
- 4. Implementing the new modified DWR TFPC assay;
- 5. Testing correlations of surrogate measurements for TFPC;
- 6. Developing and implementing studies for controlling DOC in drainage by reducing water applications for irrigation, leaching, and waterfowl habitat or by changing land use;
- Applying information from this study for assessing the impacts on Delta drinking water supplies from proposed channel modifications, drought, wetland projects, upstream release schedules, sea water intrusion, levee breaks, precursor sources, and water quality standards for the Delta; and
- 8. Making MWQI data available on DWR's California Data Exchange Center (CDEC).

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GLOSSARY

agricultural drainage Surface and subsurface waters that are collected from irrigated fields and discharged into adjacent waterways.

analytes Those constituents that are measured by laboratory analysis.

BAT Best Available Technology

connate water Highly saline water trapped underground and of marine origin.

DBP Disinfection byproducts are byproduct chemicals formed during the disinfection process.

DOC Dissolved organic carbon is the amount of measured organic carbon in the liquid portion of a liquid sample that passes through a 0.45 micron pore sized filter.

EC Electrical conductivity or specific conductance

HAA5 The total concentration of five haloacetic acid compounds specified in the D-DBP Rule.

humic substances Natural organic matter that imparts a yellowish brown color in water.

NOM Natural Organic Matter refers to organic matter that occurs naturally of biologic origin.

POC Particulate organic carbon is the amount of measured organic carbon that is trapped by a 0.45 micron pore sized filter.

precursors Chemicals that lead to the formation of other chemical compounds.

saltwater intrusion Sea water entering the estuary and fresh water region of a bay due to tidal movement or reduced river outflow.

specific absorbance The ratio of the ultraviolet absorbance of a water sample measured at the 254 nm wavelength to the dissolved organic carbon concentration.

TFPC Trihalomethane formation potential carbon is the amount of carbon computed from the total trihalomethane concentrations.

THMFP Trihalomethane formation potential is a measure of the amount of trihalomethanes (THM) that are formed after chlorinating a water sample.

TOC Total organic carbon is the total amount of measured carbon in a sample.